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**FABRICATION AND EVALUATION OF GRAPHITE FIBER-REINFORCED  
POLYIMIDE COMPOSITE TUBE FORMS USING MODIFIED  
RESIN TRANSFER MOLDING**

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by

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## INTRODUCTION

Composite materials are composed of a reinforcing fiber and a matrix binder. The purpose of the matrix, generally an organic polymer, is to transfer stress and loads from one fiber to all adjacent fibers, maintain the fibers in the proper orientation to the loads and produce a fully dense structure of the necessary shape, binding the constituents, provide environmental and thermo-oxidative stability, and perhaps most importantly, provide processability. A matrix material should also have a low density so that the composite parts will be strong and lightweight. As composite materials have become more common, the need for resins that can withstand high temperature service, that is, temperatures above 316°C (600°F), has become increasingly apparent. These resins would offer a long service lifetime for structural applications in hostile aerospace applications. Polyimides, produced by the chemical reaction of an aromatic dianhydride and an aromatic diamine, were the first of the aromatic thermally stable polymers. Serafini *et al.* (1972) developed a novel process for a high temperature polyimide resin known as PMR-15 (for *in situ* Polymerization of Monomer Reactants, the 15 represents a molecular weight of 1500) in which monomers are dissolved in a suitable carrier solvent into which the fiber cloth could be dipped and then 'laid-up' in an open-faced mold. The solvent is then evaporated, leaving the monomers, and the cure cycle is completed.

Although this method produces very good parts and has been used commercially for over twenty years, there are some drawbacks. The major problem with the resin is one of the monomer constituents of PMR-15: 4,4'-methylene dianiline (MDA), also called p,p'-diaminodiphenylmethane. MDA is toxic by inhalation or contact with the skin and is a suspected human carcinogen, regulated by OSHA, and therefore active research is under way to find a replacement for this aromatic diamine component. Recent studies at NASA Lewis Research Center in Cleveland, Ohio have indicated that 2,2-Bis[4-(4-Aminophenoxy)phenyl]propane, or BAPP (also known as 4,4'-[(1-Methylethylidene)-Bis-(4,1-Phenyleneoxy)]Bis-Benzenamine) may be a viable substitute for the MDA component of the mixture. BAPP has not been regulated

by OSHA and is considered non-hazardous and non-mutagenic. This reformulation of the PMR-15 resin system, replacing the MDA with BAPP, has been given the name AMB-21. This study will work exclusively with this newer, safer formulation.

To form a composite material from the carbon fibers a matrix must be placed in, through, and around the individual strands of the carbon fibers. Several different methods have been devised to accomplish this, such as coating the cloth with resin and 'laying-up' by hand or applying a compressive force by autoclave or press, dipping the tows in resin and then filament winding them into a cylindrical or spherical shape, or placing the fibers into an enclosed mold cavity and pumping the resin through the fibers, a process known as Resin Transfer Molding (RTM).

In normal resin transfer molding, the thermoset resin is mixed with a catalyst and then transferred at low viscosity using low pressure, possibly with the aid of a vacuum, into the enclosed mold in which the fiber reinforcement has already been placed. The PMR type resins, including AMB-21, require a modification of the normal technique because the solvent carrier fluid must be evaporated from the monomer solution at a relatively low temperature before the imidization and cure cycle can begin. This evaporation cannot take place in a fully enclosed mold cavity, some allowances must be made to remove the solvent.

## **RESEARCH OBJECTIVES**

The research objectives of this study can be broadly summarized by the following objectives: (1) prepare a solution of AMB-21 polyimide resin with a viscosity suitable for resin transfer molding; (2) design and construct a mold for the fabrication of a thin-walled composite tube suitable for Resin Transfer Molding; (3) develop a method for the manufacture of a thin-walled composite tube using Resin Transfer Molding with carbon fiber braided preforms and AMB-21 resin; (4) determine both the physical properties of the neat resin and the mechanical properties of the composite tubes by conducting various tests.

## EXPERIMENTAL METHODOLOGY

To meet the research objectives, we developed a detailed experimental plan for AMB-21 resin preparation. The resin was characterized by TGA and DSC. Viscosity measurements were also made to evaluate the suitability for resin transfer molding. A special mold (consisted of an outer mold assembly and a bladder insert) was designed and assembled for resin transfer molding of AMB-21. The fabricated thin-walled AMB-21/carbon fiber composite tubes were tested for mechanical strengths, and fiber volume contents.

## EXPERIMENTAL RESULTS & DISCUSSIONS

The resin was formulated using commercially available monomers or monomer precursors and dissolved in a mixture of methyl alcohol and acetone. The viscosity of the resulting monomer solution was checked by use of a Brookfield rheometer and adjusted by adding acetone to an easily pumpable viscosity of less than 1000 centipoise. The preparation of the resin will be described and data for the viscosity versus amount of acetone will be presented. In addition, several types of chromatographic and thermal analyses were also performed on the neat resin to investigate the components of the resin and the progression of the cure as the temperature was increased, and this data will be presented and explained.

The purpose of this study was to fabricate thin-walled carbon-fiber/polyimide composite tubes using a novel resin transfer molding technique that allows for the evaporation of solvent from a semi-closed mold cavity to form a "prepreg" by the use of removable covers over parts of the mold. The mold design also allowed for the application of vacuum to the prepreg section to facilitate removal of condensation by-products while pressure was simultaneously applied to the prepreg by an internal bladder to consolidate the finished part. A proprietary blend silicone rubber-based internal bladder was purchased and sealing caps were designed and constructed to provide the necessary 200 psi pressure for the addition step of the cure cycle. Steel shim stock placed between the bladder and the preform provided a smooth wall to the inside diameter of the

finished tube while also protecting the bladder from puncture. The study investigated the effects of time and temperature on the cure cycle of the resin, established a minimum thickness for the steel shim stock and developed techniques for the insertion of the bladder material at the proper time for consolidation. The design of the mold as well as the associated plumbing will also be described.

The finished tubes were then subjected to specific gravity measurements before any mechanical testing was done. Mechanical testing included both tension and torsion testing on a biaxial MTS test frame. Small sections were then cut out of the broken tubes and the fiber volume of the samples was determined by an acid digestion method. One small section of tube was sent to NASA Lewis Research center in Cleveland, Ohio where glass transition data was obtained both before and after a post-cure cycle. Weight loss data of this sample will also be presented.

Although this study dealt exclusively with the AMB-21 polyimide, the results may be applicable to other resin systems that can be dissolved in a suitable solvent carrier, enabling the use of the resin transfer molding technique on resin systems that could not previously be pumped into a mold at room temperature, or even at elevated temperatures. The techniques developed during this study may have broad application for the fabrication of geometrically complex composite parts, not just simple flat panels or tubes.

The work reported in this report is detailed in a masters thesis of Daniel B. Exum (1997) and is enclosed for further reference.

## References

Serafini, T.T., Delvigs, P., and Lightsey, G.R., "Thermally Stable Polyimides from Solutions of Monomer Reactants," *Journal of Applied Polymer Science*, 16 (4): 905 (1972).

Exum, D.B., "Fabrication and Evaluation of Graphite-Reinforced Polyimide Composite Tube Forms Using Modified Resin Transfer Molding," MSE Thesis, North Carolina A&T State University, Greensboro, North Carolina (1997).

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POLYIMIDE COMPOSITE TUBE FORMS USING MODIFIED RESIN  
TRANSFER MOLDING**

by

Daniel B. Exum

A thesis submitted to the graduate faculty  
in partial fulfillment of the requirements for the degree of  
MASTER OF SCIENCE

Department: Chemical Engineering

Major: Chemical Engineering

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1997

Graduate School  
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This is to certify that the Master's thesis of

Daniel B. Exum

has met the requirement of North Carolina  
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## Abstract

Exum, Daniel B. Fabrication and Evaluation of Graphite Fiber-reinforced Polyimide Composite Tube Forms using Modified Resin Transfer Molding. (Under the direction of Dr. Shamsuddin Ilias

Polyimides, produced by the chemical reaction of an aromatic dianhydride and an aromatic diamine, are aromatic thermally stable polymers capable of sustained use above 500 °F and short term use at temperatures approaching 1000 °F, making high strength, light weight composite materials possible for use in high temperature applications. PMR-15, a commercially available polyimide, has been used as a polymer matrix material for many years in hand lay-up and autoclave molding but does not lend itself to resin transfer molding because of the problem of removing the condensation polymerization by-products from the enclosed mold cavity. Recent studies at NASA Lewis Research Center in Cleveland, Ohio have indicated that 2,2-Bis[4-(4-Aminophenoxy)phenyl]propane, or BAPP (also known as 4,4'-[(1-Methylethylidene)-Bis-(4,1-Phenyleneoxy)]Bis-Benzenamine) may be a viable substitute for the MDA component of the mixture. The research objectives of this study can be broadly summarized by the following objectives: (1) prepare a solution of AMB-21 polyimide resin with a viscosity suitable for resin transfer molding; (2) design and construct a mold for the fabrication of a thin-walled composite tube suitable for Resin Transfer Molding; (3) develop a method for the manufacture of a thin-walled composite tube using Resin Transfer Molding with AS4 braided carbon fiber preforms and AMB-21 resin; (4) determine both the physical properties of the neat resin and the mechanical properties of the composite tubes by conducting various tests. The techniques developed during this study may have broad applications for the fabrication of geometrically complex composite parts, not just simple flat panels.



## **DEDICATION**

This thesis is dedicated to my loving wife Jenny, whose support and encouragement during my many periods of self-doubt provided the determination to keep trying, no matter how hopeless the situation appeared. I hope the results justify the effort.

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Background on Composite Materials

Composite materials have been used for centuries. In prehistoric and biblical times, straw was added to clay in the making of bricks to give the clay additional strength. This is one of the first examples of a composite structure, defined by Pebly (1987) as a combination of two or more materials (including reinforcing elements, fillers, and composite matrix binder), differing in form or composition on a macroscale. The constituents act in concert and retain their identities, without dissolving or merging completely into one another, meaning that the components can be physically identified and exhibit an interface between one another. The clay in the brick acted as the matrix material while the straw was a reinforcing element, providing strength to keep the brick from crumbling under loads. The two constituents act synergistically to yield a substance much stronger and tougher than plain clay or straw.

In recent years typical reinforcing elements for structural applications have been fibers of glass, boron, Kevlar™ or other aramids, or graphite, a form of carbon (Smith and Zweben, 1987). Of these, the highest strengths and greatest stiffness are exhibited by the fibers of graphite in the direction parallel to the length of the fibers. Unidirectional graphite fiber-reinforced epoxies provide a specific tensile strength (ratio of material strength to density) that is four to six times greater than steel or aluminum, and a specific modulus (ratio of material stiffness to density) that is three to five times greater than steel

or aluminum. These properties allow graphite fiber-reinforced composites to be built that are 25-45% lighter than aluminum structures designed to the same structural requirements, an important factor to the military, transportation and sporting goods industries. These properties are derived directly from the characteristics of the covalent carbon-carbon bond, which in the hexagonal array of the graphitic form of carbon are the strongest chemical bonds known (Blakeslee *et al.*, 1970). The manufacture of carbon fibers began in the 1960's, and although the price was exorbitant, large quantities of nearly defect free material were available by the end of the decade. These fibers, micron-sized and highly oriented, are now available in standard bundles or "tows" of 3000 (3K), 6000 (6K), or 12,000 (12K) individual fibers wound without a twist on a cardboard core. These cores are placed on a loom or braiding machine to make fabric or used in multi-axial braiding machines to form a three-dimensional 'preform'.

The matrix is the other necessary constituent of a composite material, and it is generally an organic polymeric material. The purpose of the matrix is to transfer stress and loads from one fiber to all adjacent fibers, maintain the fibers in the proper orientation to the loads and produce a fully dense structure of the necessary shape, binding the constituents, provide environmental and thermo-oxidative stability, and perhaps most importantly, provide processability. A matrix material should also have a low density so that the composite parts will be lightweight. As composite materials have become more common, the need for resins that can withstand high temperature service above 316 °C (600 °F) has become increasingly important. These resins would offer a long service

lifetime for structural applications in hostile aerospace applications. Polyimides, produced by the chemical reaction of an aromatic dianhydride and an aromatic diamine, were the first of the aromatic thermally stable polymers. Discovered in 1908, polyimides were so difficult to process and had such poor mechanical and physical properties that little could be made from these polymers until a breakthrough discovery in the early 1970's. Serafini *et al.* (1972) developed a novel process for a high temperature polyimide resin known as PMR-15 (for *in situ* Polymerization of Monomer Reactants, and 15 represents a molecular weight of 1500) in which monomers are dissolved in a carrier solvent into which the fiber cloth could be dipped and then 'laid-up' in an open-faced mold. The solvent is then evaporated, leaving the monomers, and the cure cycle is completed. This technique was quickly commercialized by companies that sold pre-impregnated and dried cloth, termed 'pre-preg', that could be cut and layed-up without having to add the monomeric resins.

Although this method produces very good parts and has been used commercially for over twenty years, there are some drawbacks. The major problem with the resin is one of the monomer constituents of PMR-15: 4,4'-methylene dianiline (MDA), also called p,p'-diaminodiphenylmethane. MDA is toxic by inhalation or contact with the skin and is a suspected human carcinogen, regulated by OSHA, and therefore active research is under way to find a replacement for this aromatic diamine component. Recent studies at NASA Lewis Research Center in Cleveland, Ohio have indicated that 2,2-Bis[4-(4-Aminophenoxy)phenyl]propane, or BAPP (also known as 4,4'-[(1-Methylethylidene)-Bis-(4,1-Phenyleneoxy)]Bis-Benzenamine) may be a viable substitute for the MDA component

of the mixture. BAPP has not been regulated by OSHA and is considered non-hazardous and non-mutagenic. This reformulation of the PMR-15 resin system, replacing the MDA with BAPP, has been given the name AMB-21.

To form a composite material from the carbon fibers a matrix must be placed around the individual strands of the carbon fibers. Several different methods have been devised to accomplish this, such as coating the cloth with a resin solution and 'laying-up' by hand and heating under a compressive force using an autoclave or press, dipping the cloth in resin and then filament winding into a cylindrical or spherical shape, or placing dry fibers into an enclosed mold cavity and pumping the resin through the fibers, a process known as Resin Transfer Molding (RTM).

In normal resin transfer molding, the thermoset resin is mixed with a catalyst and then transferred at low viscosity using low pressure, possibly with the aid of a vacuum, into the enclosed mold in which the dry fiber reinforcement has already been placed. The PMR type resins, including AMB-21, require a modification of the normal technique because the solvent carrier fluid must be evaporated from the monomer solution at a relatively low temperature before the imidization and cure cycle can begin. This evaporation cannot take place in a fully enclosed mold cavity, some allowances must be made to remove the solvent in order to create a 'prepreg', an industry term for cloth or preform that has been pre-impregnated with resin and is ready to be thermally cured.

## 1.2 Research Objectives

The primary purpose of this study was to fabricate and test thin-walled graphite fiber-reinforced/polyimide composite tubes using a novel resin transfer molding technique that allows for the evaporation of solvent from a semi-closed mold cavity to form a “prepreg” by the use of removable covers over parts of the mold. The mold design also allowed for the application of vacuum to the prepreg section to facilitate removal of imidization products while pressure was simultaneously applied to the prepreg by an internal bladder to consolidate the finished part. The objectives of this study can be broadly summarized by the following: (1) prepare a solution of AMB-21 polyimide resin with a viscosity suitable for resin transfer molding; (2) design and construct a mold for the fabrication of a thin-walled composite tube; (3) develop a method for the manufacture of a thin-walled composite tube using braided carbon fiber preforms and AMB-21 resin; (4) determine the physical and mechanical properties of the composite tubes by conducting various tests.

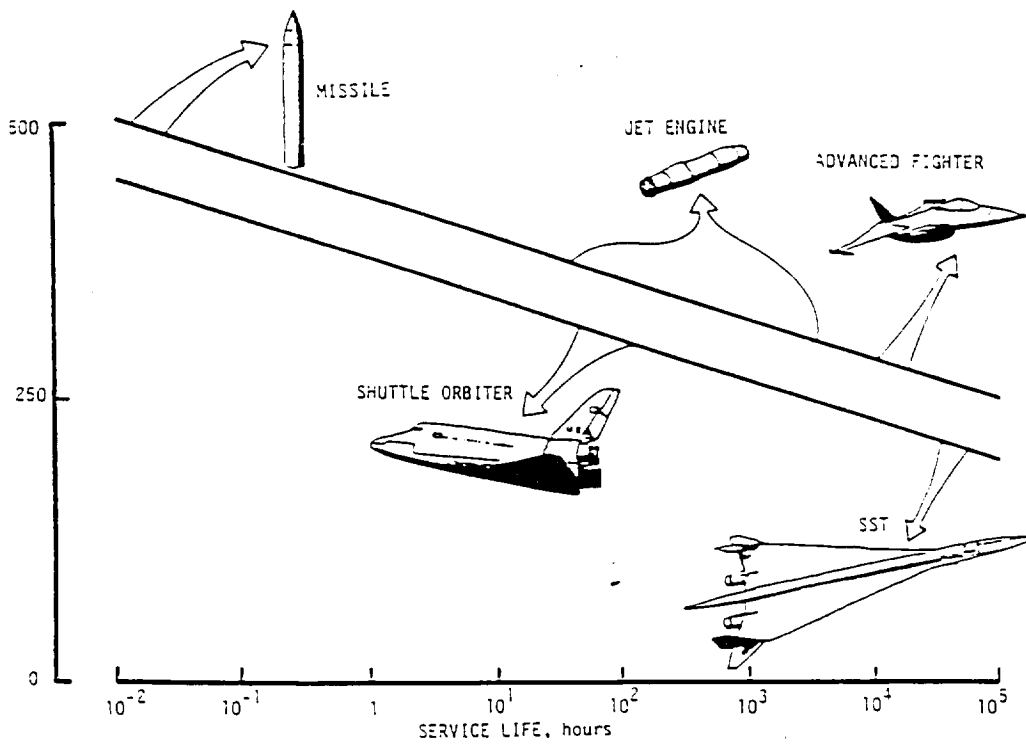
Although this study dealt exclusively with the AMB-21 polyimide, the results may be applicable to other resin systems that can be dissolved in a suitable solvent carrier, enabling the use of the resin transfer molding technique on resin systems so viscous that they could not previously be pumped into a mold at room temperature, or even at elevated temperatures. The techniques developed during this study may have broad application for the fabrication of geometrically complex composite parts, not just simple flat panels or tubes.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.0 Introduction

Epoxy resins are the most widely used polymer matrix materials for advanced composite materials, offering ease of processing and excellent physical and mechanical properties. One limitation of epoxy resins is that their upper-use temperature is approximately 177 °C (350 °F) because of thermal stability and the glass transition temperature. Although adequate for most earth-bound sporting goods applications, this upper-use temperature is far below what is necessary for the stringent demands of many high performance aerospace applications, which may be subjected to continuous use temperatures of 300 °C (572 °F) or higher. Material scientists have been striving for many years to formulate a resin with the easy processibility of epoxies that could withstand the rigorous temperature extremes imposed on engineered materials in jet engines and rocket motors as well as in the high speed environment of ballistic missiles, supersonic aircraft, and spacecraft. St. Clair and St. Clair (1984) expect the service life for such materials to range from the single flight of a missile lasting only a few minutes at temperatures approaching 500 °C (932 °F) to the supersonic transport which will require at least 50,000 hours of cumulative service at 177-232 °C (350-450 °F), as shown in figure 2.1. This chapter will present a brief history of the development of temperature-resistant polyimide resins, a discussion of the complex polymerization chemistry involved with the PMR type resins, and an overview of



2.1: Time and temperature needs of advanced materials.

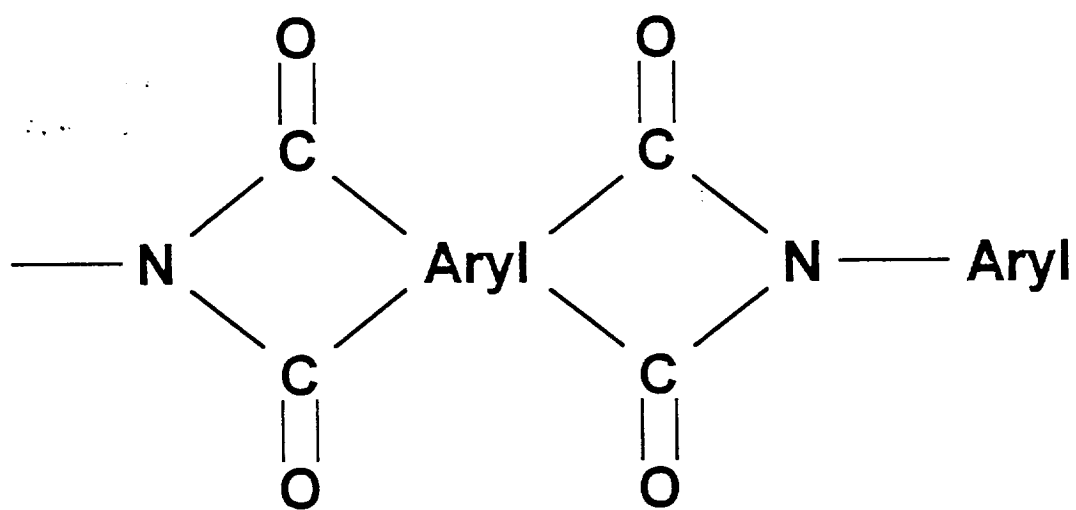
processing techniques, in particular autoclave molding and Resin Transfer Molding (RTM).

## 2.1 History and Chemistry of Polyimide Resins

Polyimides have been known for decades, but they were so difficult to process that nothing useful could be made from them. This section will present a brief history of the development of these temperature-resistant compounds, noting some of the breakthrough achievements responsible for improving the processability of the class, particularly the PMR-type resins. The major advances in the processibility of some of the polyimides will be illustrated and explained with chemical structure.

The word polyimide is a generic designation and refers to a class of long-chained polymers which have repeating imide groups (defined as a nitrogen containing acid having two double bonds) as an integral part of the main chain. The polyimide chains consist of carbon-only aromatic rings, sometimes called aryl groups, alternated with heterocyclic groups, which are ring-type structures containing other elements in addition to carbon (see Figure 2.2). By varying the monomeric starting materials, that is, changing the aryl groups, polyimides of different chemical composition, structure, degree of cross-linking and ease of processibility can be obtained. In terms of chemistry, there are two general types of commercial polyimides: thermoplastic or linear polyimides, derived from a condensation reaction between anhydrides or anhydride derivatives and diamines with subsequent evolution of volatile products, and





**Figure 2.2:** General repeating structure of a Polyimide.

cross-linked thermosetting polyimides, formed by an addition reaction between unsaturated groups of the preformed imide monomers or oligomers. The imide monomers or oligomers are previously derived from a typical condensation reaction, but final polymerization occurs because of the addition reaction, with no evolution of volatiles during the final stage (Scola, 1987).

The polyimides are characterized by a high degree of rigidity and excellent thermal stability due to multiple bonds between the aromatic and/or heterocyclic functional groups and subsequent cross-linking between chains, effected by the reactive end-caps of the oligomer chains. These ring type structural units are able to absorb thermal energy and contain a minimum number of oxidizable hydrogen atoms which promotes temperature resistance (Serafini, 1987). In addition, polyimides have a high radiation stability and can withstand exposure to neutrons, electrons, ultraviolet light, and gamma radiation. At the decomposition point, the thermosets crumble to a fine powder without melting (Fusaro, 1984). Polyimides are also extremely resistant to most organic solvents, including aliphatic hydrocarbons, ether, ketones, aromatic hydrocarbons, and chlorinated aliphatic and aromatic hydrocarbons. Polyimides are, however, hydrolyzed in strong acids and strong bases, including aqueous hydrazine solutions, at elevated temperatures (Scola, 1987).

In addition to, and because of, their resistance to elevated temperatures, polyimides are also resistant to being processed into useful structural components. The molecular building blocks that are responsible for the thermal stability of high-

temperature polymers are also responsible for their inherent insolubility and infusibility, commonly referred to as intractability. Until the early 1970's, the intractable nature of polyimides, which in theory could provide a one hundred percent increase in continuous use-temperature, has prevented the realization of the full potential of these polymers as matrix resins for high temperature polymer matrix composites (Serafini, 1984). The poor processing characteristics of early high-temperature polymers prevented them from performing the necessary functions of a matrix material. Composites fabricated with these early matrices exhibited high void contents, poor translational efficiencies between fibers, depressed elevated-temperature mechanical properties, and inferior thermo-oxidative stabilities. The major emphasis of early research work on polyimides was to improve the thermal stability of the polymers, and little work was done before 1970 to improve the processibility of the formulations (Serafini, 1987).

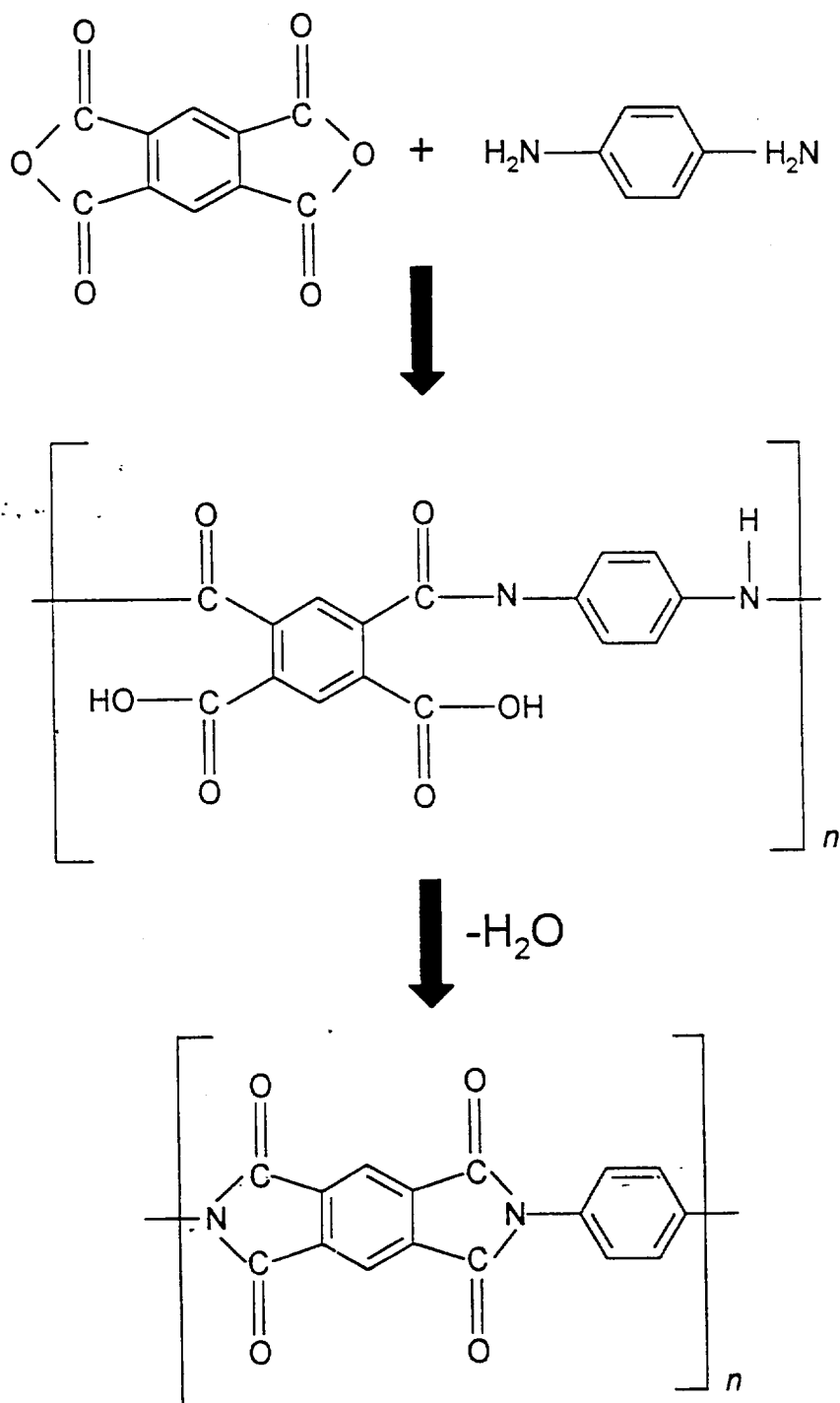
High-temperature laminating resins of the class known as condensation-type polyimides were first used in structural composite components in the early 1960's. These polymers are also sometimes referred to as linear polyimides because of the long backbone chain with minimal cross-linking. First discovered early in the century by Bogert and Renshaw (1908), it was not until the mid nineteen-fifties that the polymers were made practical by Edwards and Robinson (1955). The impetus behind their development was the supersonic transport program. Although these materials presented processing difficulties in the manufacture of laminates, they had good high-

temperature properties along with cost and availability advantages. It was relatively easy to make the laminating resins commercially available at a reasonable cost because the same monomers were being used in versions for other product forms such as film and wire enamels (Serafini, 1987).

Condensation-type polyimides are derived from polyamic acids, which are produced by a series of step growth reactions at room temperature from a dianhydride or dianhydride derivative and a diamine. Condensation-type aryl polyimides are generally prepared by reacting aromatic diamines with aromatic dianhydrides, with aromatic tetracarboxylic acids, or with dialkyl esters of aromatic tetracarboxylic acids. The diamine-dianhydride reaction is preferred for preparing films and coatings, whereas the latter two combinations of reactants are generally employed for the preparation of matrix resins (Serafini 1984). Traditionally, these linear polyimides have been processed in the polyamic acid form, because once converted to the polyimide they become intractable and precipitation would occur during intermediate stages of the polymerization. To circumvent this problem, the condensation is performed in two stages. The usual preparation of a linear aromatic polyimide involves the reaction of an aromatic dianhydride with an aromatic diamine in a high-boiling point solvent such as *N*-methyl-2-pyrrolidone (NMP) at temperatures below 70 °C (158 °F) to produce a high molecular weight, soluble polyamic acid. The long chain polyamic acids are next fabricated into a suitable form then cyclized (imidized) to an insoluble and thermally stable polyimide by chemical conversion at ambient temperature or by heating at a high

temperature (300 °C or 572 °F) to drive off both the solvent carrier and the products of the condensation reaction (see Figure 2.3). These thermoplastic polyimides are rigid, high-melting, thermally stable materials. Some flexibility can be introduced into the polymer structure by the use of diamines which contain a flexible linkage unit such as 4,4'-diaminodiphenyl ether,  $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{NH}_2$  (Allcock and Lampe 1981).

All of the early polyimide resins were the condensation reaction-type, needed a one-stage cure, and gave off copious amounts of water. The solvent used to put the powdered resin in solution was NMP, which is extremely difficult to remove because of its high boiling point and low vapor pressure. If the solvent was not removed before the resin solidified, the resin precipitation would occur to yield laminates with very low strength. To further complicate the situation, an arsenic catalyst was employed, which is considered unacceptable under the current regulations of the Occupational Safety and Health Administration. These resins were easily cured, requiring only 340kPa (50 psi) and full vacuum in an autoclave, and 177 °C (350 °F) curing temperatures. The resins reached their high temperature capability (280 °C or 535 °F) by means of an extended postcure at 288 °C (550 °F). Unfortunately, they produced laminates that were extremely high in void content (approximately 9 volume percent) and consequently susceptible to moisture pick-up, which lowers the glass transition temperature of the component significantly. Aircraft companies have since used this tendency toward high void content to produce the sound suppression panels



**Figure 2.3:** Preparation of a linear aromatic polyimide.

around jet engines. Condensation reaction-type polyimides continue to be used in various acoustic applications (Mace, 1987).

Serafini (1987) attributes the major problems in processing condensation-type polyimide prepreg materials both to the inherent nature of condensation reactions with condensate by-product evolution and to the use of solvents with high boiling points, which are difficult to remove and lead to void content problems. During thermal processing of the prepreg to effect chain growth and solvent/by-product removal, appreciable imidization also occurs, viscosity of the resin increases, flow decreases, and the resin converts to an intractable state. Reduced resin flow inhibits the already difficult removal of the last traces of the solvent and volatile by-products. The entrapment of these volatile materials results in composites having void contents in the range of 5 to 10 volume %, particularly for thick sections (>1mm, or 0.04"). Although industry specifications generally allow no more than 2% voids, a good cure cycle for composites usually results in void content substantially less than 1% (Konarski, 1987). The presence of these voids adversely affects mechanical and thermo-oxidative stabilities of the composite.

Konarski (1987) presents several causes of disproportionate void formation, such as excessive bleeding, resin starvation and the presence of volatiles remaining in the resin at the point of gelation. To minimize the formation of voids caused by volatiles present in the resin, Konarski recommends a slower heat-up rate or an intermediate hold at a time of low viscosity, which permits the volatiles time to diffuse

through the resin and escape. Minimal pressure vacuum should be held until after this hold period. Waiting too long to apply pressure during the cure cycle can also lead to the formation of voids. If the cure of the resin has advanced too far, the application of pressure will not give the compaction necessary to produce a good part. By evaluating the viscosity curves and adjusting the cure cycle accordingly, Konarski suggests that the problems of excess void formation can be minimized.

Research on linear polyimides has yielded an interesting thermoplastic linear polyimide film adhesive named LARC-TPI. Developed by NASA Langley Research Center in 1980, the resin is a linear thermoplastic polyimide which can be processed in the imide form to produce large-area, void-free adhesive bonds. Thermoplastic resins are materials that are already fully polymerized in a linear fashion, as opposed to the three-dimensional nature of thermosets. Their high temperature properties are achieved through backbone stiffness, whereas thermosets achieve their properties through their high degree of cross-linking. Unlike conventional polyimides, LARC-TPI is imidized and freed of condensation by-products and solvent prior to bonding. Its thermoplastic nature is undoubtedly due to the structural flexibility introduced by bridging groups in the monomers and by the use of a *meta*-linked diamine: 3,3'-(*m,m'*)-DABP as shown in Figure 2.4 (St. Clair and St. Clair, 1984). The advantages and disadvantages of thermosets and thermoplastics are summarized in Table 1. The primary advantage of thermoplastics lies in the fact that they are already fully reacted. Subjecting them for a brief time to a temperature above their softening point will cause



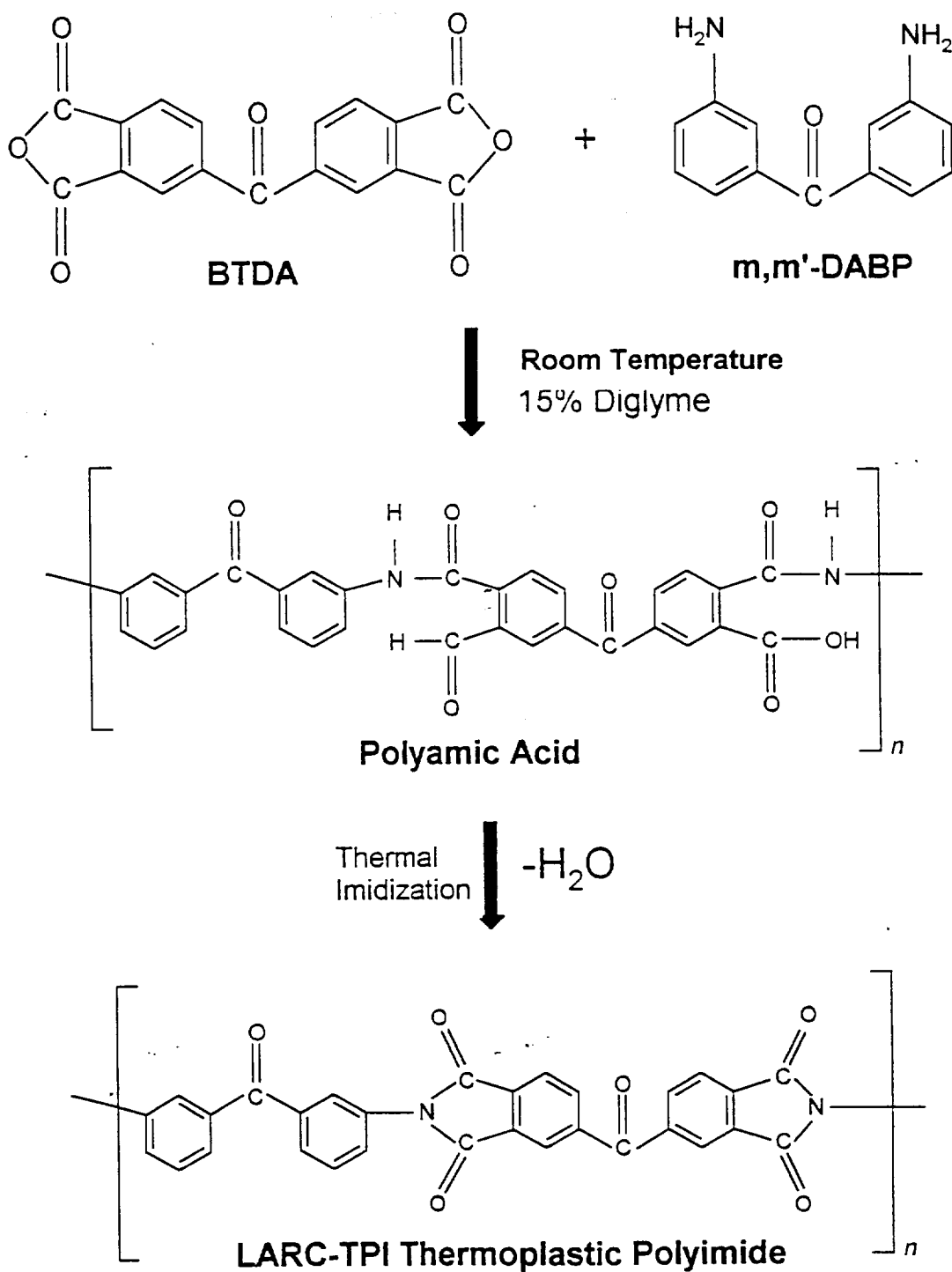


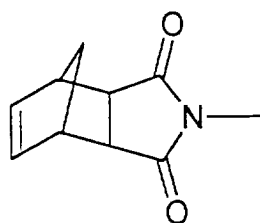
Figure 2.4: Preparation of LARC-TPI polyimide.

**Table 2.1:** Subjective assessment of Thermoset and Thermoplastic processing  
(Muzzy and Kays, 1984).

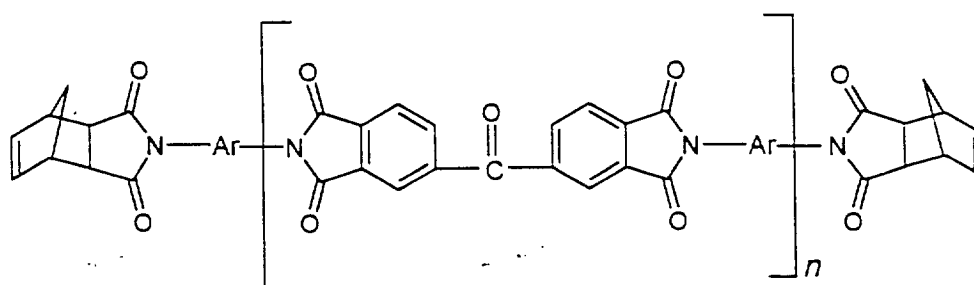
Aspect	Advantage	Reason
<b>Prepreg formation</b>		
Viscosity	Thermoset	Lower
Solvents	Thermoset	Greater choice
Hand	Thermoset	More flexible
Tack	Thermoplastic	Prepolymer variable
Storage	Thermoplastic	Not reactive
Quality control	Thermoplastic	Fewer variables
<b>Composite fabrication</b>		
Lay-up	Thermoset	Ease of Handling
Degassing	Thermoplastic	Fewer volatiles
Temperature changes	Thermoplastic	Fewer
Maximum temperature	Thermoset	Lower
Pressure changes	Thermoplastic	Fewer
Maximum pressure	Thermoset	Lower
Cycle time	Thermoplastic	Lower
Postcure cycle	Thermoplastic	Not required
Repair	Thermoplastic	Remelt
Post forming	Thermoplastic	Remelt

them to melt and fuse. In the case of thermosets, a long time is needed to react the molecules and achieve the fully cured state. Thermoplastics require heat and pressure for a brief time at the softening or melting point, followed by pressure cooling below the melting point (McCarvill, 1987). Additional studies have shown that the upper-use temperature of linear polyimide resins can be extended by the addition of small amounts of AL (III) ions (St. Clair and St. Clair, 1984).

Attempts were made to alleviate the processing difficulties associated with high-temperature linear polyimides through the use of addition-type polymer chemistry. A major advance in the chemistry of high temperature resins was the development of a novel class of polyimides which cure by an addition reaction instead of the condensation reaction of previous methods (St. Clair and St. Clair, 1984). Addition polymers are easily processed in the form of short-chained oligomers which thermally chain extend by an addition polymerization involving reactive and unsaturated end groups. In the late 1960's TRW scientists developed a route for preparing short-chained, low molecular weight amide-acid (polyimide) pre-polymers with reactive and unsaturated end-caps of 5-norbornene-2,3-dicarboxylic (nadic) anhydride as shown in Figure 2.5, which polymerized into thermally stable polyimides without the evolution of by-products. The final cure of this polymer, named P-13N, was effected by an addition reaction of olefinic end groups on the nadimide prepolymer to produce an essentially void-free, highly cross-linked polymer (see Figure 2.6). Unfortunately, this material had a very short and variable shelf life, with



**Figure 2.5:** Nadic Anhydride end-cap.



**Figure 2.6:** Nadic-terminated imide oligomer.

40% solids solutions sometimes gelling or precipitating in as little as two days (Serafini *et al.*, 1972).

The new addition-type chemistry exhibited by P-13N provided the impetus for what is arguably the most important contribution to the field of high-temperature organic matrix materials. Serafini, *et al.* (1972) described a new method which came to be known as *in situ* polymerization of monomeric reactants, or PMR. The PMR concept consists of impregnating the reinforcing fibers with a solution in which the monomers are dissolved in a low boiling point alkyl alcohol, such as ethanol or methanol, to enable processing. The monomers are essentially unreactive at room temperature; they are latent, as in the case of prepreg epoxy resins, reacting at high temperatures. Mace (1987) states that the addition or PMR type polyimides are cured in two stages. The first consists of solvent evaporation and an imidization reaction, which is a condensation reaction evolving water or methanol (or both) to form short chain oligomers. The second stage consists of a ring-opening addition type cross-linking reaction at the nadic end caps that is similar to a common epoxy-type reaction, but is carried out at a higher temperature, forming a thermo-oxidatively stable polyimide matrix. Because the final *in situ* reaction occurs without the release of volatile materials, high quality void-free composites can be fabricated. Note, however, that the presence of solvent, as well as the liberation of volatiles during polymerization, may create voids in the cured parts. The cure cycle and

devolatilization are critical for producing high quality parts. Serafini *et al.* (1972)

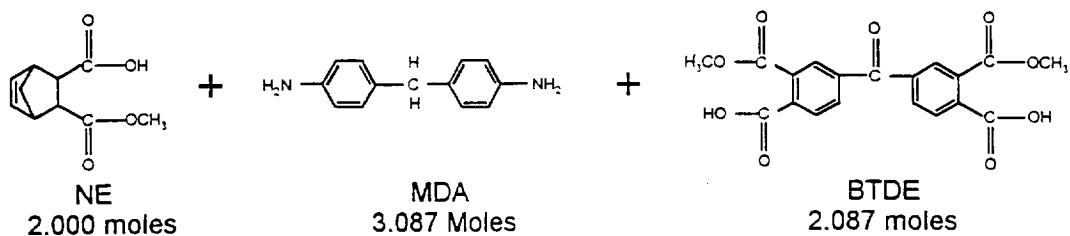
draw the following conclusions about their groundbreaking research:

- (1) Various combinations of appropriate monomers and solvents can be made into monomer reactant solutions of varying stoichiometry for the synthesis of processable polyimides having a broad range of processing characteristics and properties.
- (2) These solutions offer the following advantages over amide-acid prepolymer solutions: (a) excellent shelf life; (b) nontoxic alcoholic solvents such as methanol, which have low boiling points and are relatively easy to remove, can be used; (c) increased solubility (solutions containing 60 to 70% solids by weight are readily obtainable); (d) low solution viscosity.
- (3) There is little or no loss of the mechanical properties or thermal stability characteristics of graphite fiber-reinforced composites made from solutions of monomeric reactants compared with those of composites made from amide-acid prepolymer solutions.

One monomer solution showed particular promise, and was given the designation PMR-15. The prepolymer solution of this material consists of three monomers dissolved in methanol: monomethylester of 5-norbornene-2,3-dicarboxylic acid (NE); dimethyl ester of 3,3',4,4'-benzophenone tetracarboxylic acid (BTDE); and 4,4'-methylene dianiline (MDA), in the molar ratio 2:2.087:3.087. Although the reaction sequence can be broadly categorized into two stages, there are actually four separate and distinct steps in the formation of the polymer, as illustrated by Figure 2.7. Scola (1987) describes the first process as amide formation, which occurs between room temperature and 150 °C (300 °F). It is during this part of the cure cycle that the solvent is removed, leaving a dried "prepreg". In the second step, imidization occurs through a condensation reaction in the temperature range of 150 to  $\geq 250$  °C

### Step 1

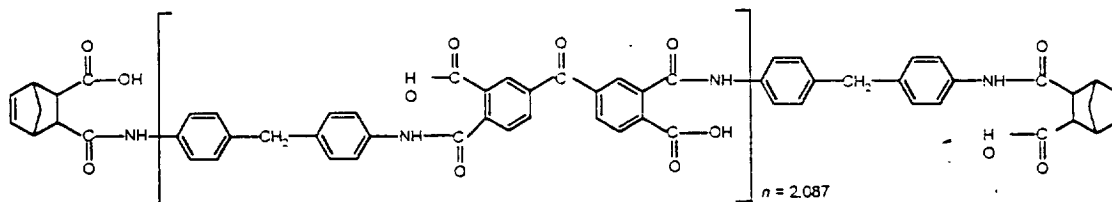
Monomers in solution



### Step 2

Amide-acid prepolymer

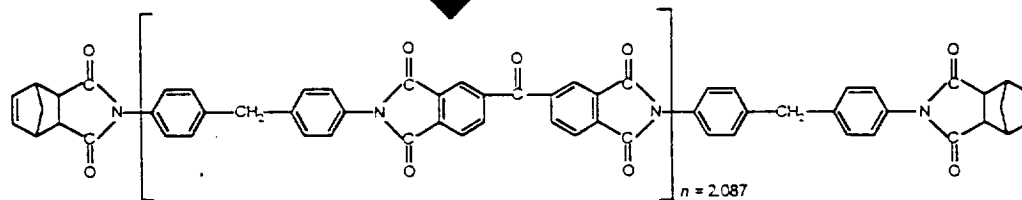
Room Temperature to 150 °C (302 °F)



### Step 3

Imidized prepolymer

150 - 250 °C (302 - 482 °F)



### Step 4

Thermally cross-linked polymer

Pressure at 250 - 316 °C  
(482 - 600 °F)

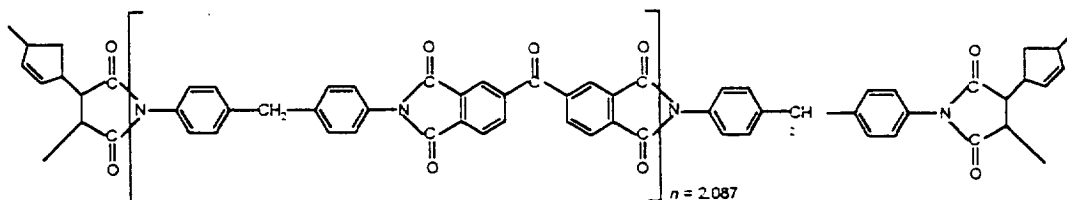


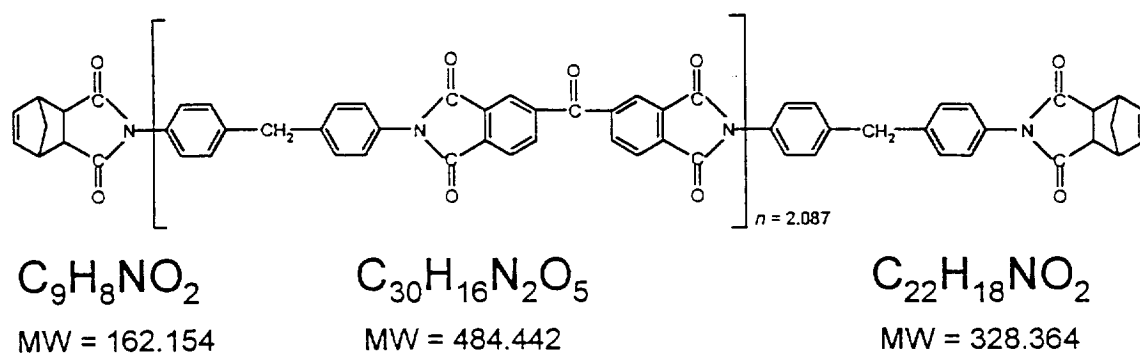
Figure 2.7: General reaction scheme for PMR-15 polyimide.

(300 to  $\geq 480$  °F), forming low molecular weight norbornenyl-endcapped oligomers. The idealized structure of a solvent-free oligomer, as well as the molecular weight of each segment, is shown in Figure 2.8. The theoretical empirical formula for this oligomer, where  $n = 2.087$ , is  $C_{93.61}H_{59.392}N_{6.174}O_{14.435}$ , yielding a formulated molecular weight (FMw) of 1501.56.

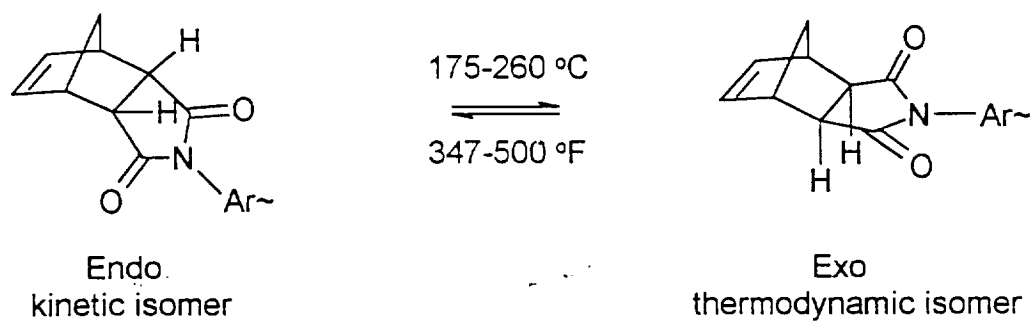
Maximovitch and Galeos (1984) stress that good control is essential in processing polyimide composites, as several physical and chemical changes can occur simultaneously during cure. During the imidization step, isomerization of the endo nadic end-capped imide oligomer (endoisomer) to the exoisomer also occurs in the temperature range of 175-260 °C (350-500 °F), further complicating the processing of the resin (see Figure 2.9). PMR-15 represents a division within the addition-curing polyimides known as the Reverse Diels-Alder (RDA) polyimides, which not only undergo the amidation and imidization reactions to form a low molecular weight oligomer, typical of condensation polyimides, but also undergo an irreversible Diels-Alder reaction leading to a high molecular weight cross-linked polyimide. These latter two reactions distinguish the RDA addition-type polyimides from the condensation polyimides.

Finally, in the fourth step, at a temperature in the range of 275-350 °C (527-662 °F), an irreversible Diels-Alder reaction of the endo/exo-oligomers occurs and the norbornenyl groups undergo a ring-opening reaction, yielding the reactive intermediate oligomers cyclopentadiene and bismaleimide, which under pressure will recombine to





**Figure 2.8:** Idealized PMR-15 polyimide oligomer structure

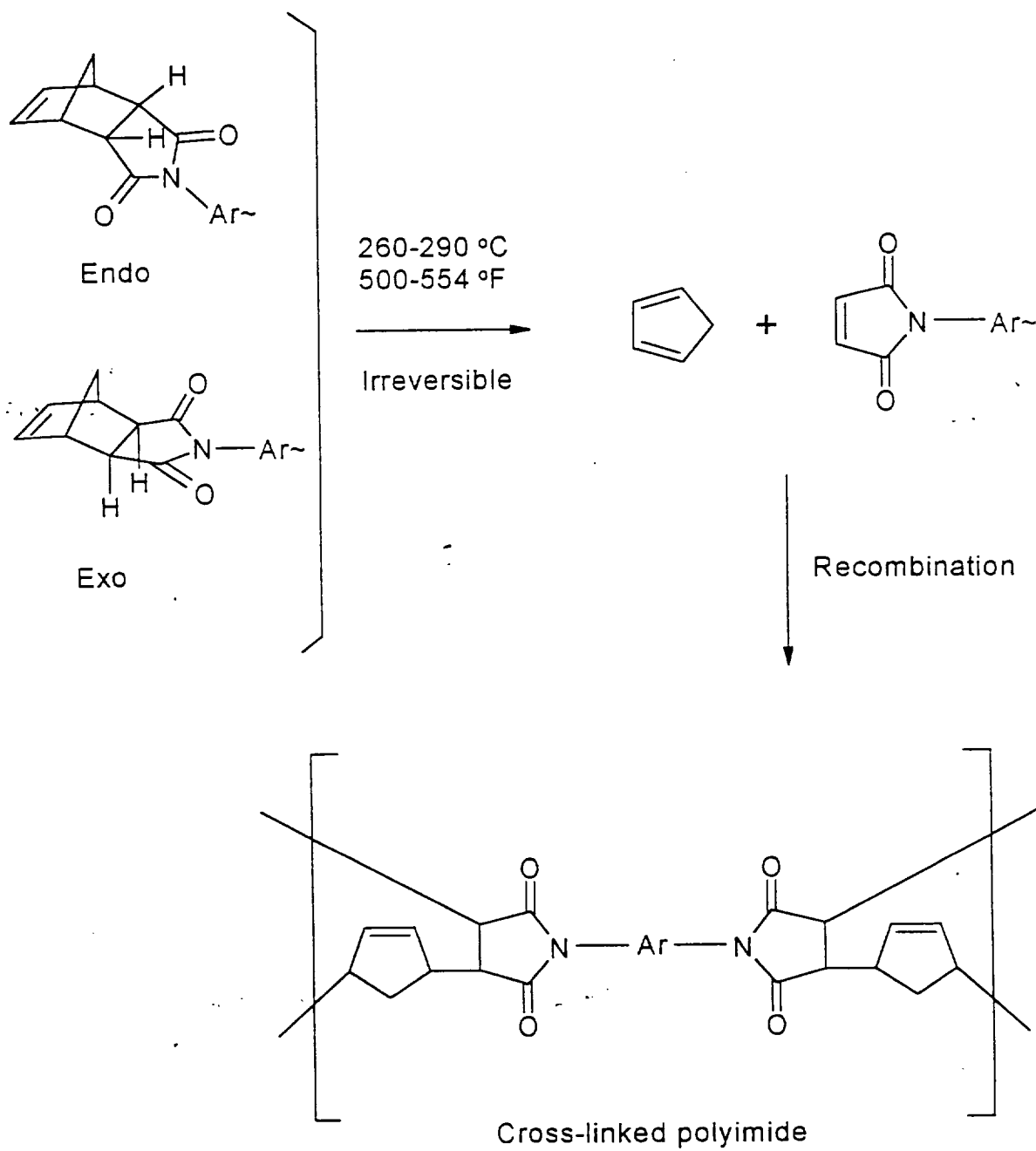


**Figure 2.9:** Isomerization during PMR-15 polymerization

yield a cross-linked polyimide with the idealized structure shown in Figure 2.10. The maleic functions immediately copolymerize with the cyclopentadiene and unreacted norbornenyl groups to form a stable crosslinked polyimide without the evolution of volatiles. External pressure, generally supplied by an autoclave or compression press, ensures that the volatile cyclopentadiene stays in the resin to react instead of forming voids. The critical steps in the processing of the polyimide are the removal of residual by-products from the imidization reaction and the removal of low molecular weight volatile components formed during the various process steps.

The response of the aerospace community was almost immediate. Prepregs, molding compounds, and even adhesives based on PMR technology have been commercially available from the major suppliers of composite materials since the mid-seventies. Several years after the publication first described the technique, Serafini (1984) states that one of the most rewarding aspects of the PMR polyimide development has been the successful demonstration of PMR-15 polyimide composite materials as viable engineering materials. Because of their commercial availability, processability, and excellent retention of properties at elevated temperature, PMR-15 composites have been used to fabricate a variety of structural components for modern aerospace requirements. These components range from small compression molded bearings to large autoclave molded aircraft engine cowlings and ducts.

The resin is not perfect, however, and St. Clair and St. Clair (1984) note that although much has been gained toward alleviating the evolution of volatiles associated



**Figure 2.10:** Reverse Diels-Alder reaction during cure.

with linear systems using the PMR method, the addition-type polyimides which have been developed are thermoset compounds which cure to form a highly crosslinked network. In comparison to a linear system, these crosslinked networks are very brittle. In addition, Scola (1987) also notes that the nadic portion of this material contains aliphatic groups which somewhat reduce the long-term thermal stability of the resulting polymer. There is also the problem of having to cure the nadic-capped imides under high pressure in order to prevent a retrograde Diels-Alder reaction from occurring which would allow the molecule to dissociate into two components, one of which (cyclopentadiene), is volatile, and may cause voids.

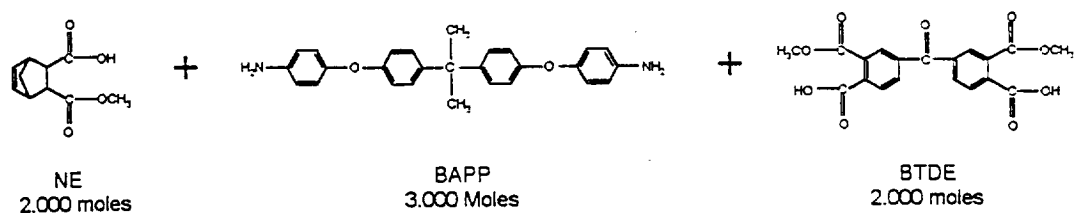
Roberts (1987) notes the important physical phenomenon of "puffing" which can result in the formation of large wrinkles in the reinforcing cloth. Puffing results in the expansion of the laminate during imidization, and is caused by the evolution of water as a condensation product. This poses no problem on thin, relatively flat parts, but it becomes acutely necessary in the case of cylinders to restrain the laminate during "puffing" in order to avoid the formation of large wrinkles.

Another problem is the toxicity of one of the monomers; MDA is a suspect carcinogen, and for this reason OSHA has proposed rigid regulations regarding the safe handling of materials containing MDA, which greatly increases the costs associated with PMR-15. For several years NASA, in conjunction with resin manufacturers and end-users, has been studying alternative formulations of the monomeric mixture in the hopes of finding a low cost combination that will provide all

of the high temperature thermo-oxidative stability of PMR-15 without the carcinogenic presence of MDA. One of the best candidates so far has been AMB-21, which uses 2,2-Bis[4-(4-Aminophenoxy)phenyl]propane (BAPP) in place of MDA in a slightly revised molar ratio of 2 moles BTDE:3 moles BAPP:2 moles NE. Vannucci and Chriszt (1995) report that AMB-21 formulation can be used as a PMR-15 resin replacement in graphite reinforced composites for extended use at temperatures up to 260 °C (500 °F) and at 288 °C (550 °F) for a maximum of 5000 hours. The BAPP monomer is readily available, low in cost, considered non-mutagenic and presently on the TOSCA approved handling list. The hypothesized reaction sequence of AMB-21 is presented in Figure 2.11.

## Step 1

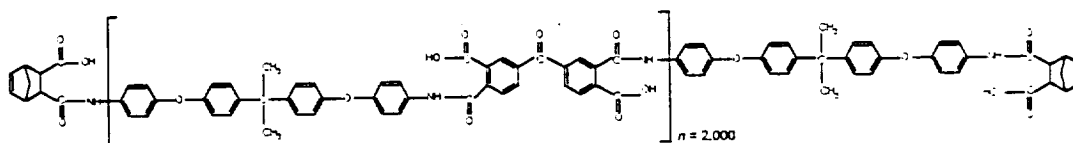
Monomers in solution



## Step 2

Amide-acid prepolymer

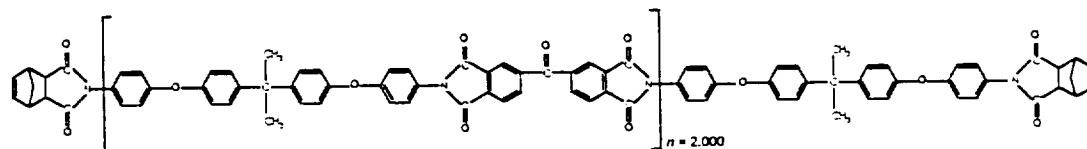
Room Temperature to 150 °C (302 °F)  
- CH<sub>3</sub>OH



## Step 3

Imidized prepolymer

150 - 250 °C (302 - 482 °F)  
- H<sub>2</sub>O



## Step 4

Thermally cross-linked polymer

Pressure at 250 - 316 °C  
(482 - 600 °F)

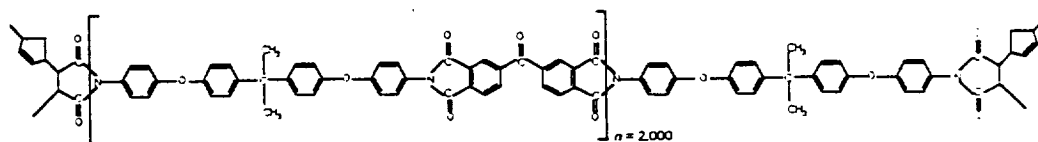


Figure 2.11: General reaction scheme for AMB-21 polyimide.

## **2.2 Processing Techniques for PMR Type Resins**

The processing of PMR-type addition-curing polyimide resins into useful composite parts has generally been accomplished by the method of autoclave molding. This section will present a brief description of this technique, as well as a discussion of the technique used in this study, Resin Transfer Molding. An examination of the viscosity and flow behavior of the melted resin will also be presented.

### **2.2.1 Autoclave Molding**

An autoclave is a closed vessel for conducting and completing a chemical reaction under heat and pressure. The heat is generally supplied by electric resistance heating coils or indirect gas-fired systems, which provide substantial operating savings over electrical systems when direct energy and demand charges are considered. The pressure is supplied by a compressed gas which exerts a compressive force on all objects inside the sealed chamber. Nitrogen is the gas most often used in autoclaves because it does not support combustion, which is particularly important at the high curing temperatures of the polyimide resins. Vacuum bulkhead connections are also standard equipment on industrial autoclaves, permitting the application of vacuum to bagged parts for the removal of volatile components evolved during the cure cycle and for the compaction of the laminate layers, which will not compact due to hydrostatic pressure alone (Taricco, 1987).

Pebly (1987) defines autoclave molding as a process in which, after lay-up, winding, or wrapping, an entire assembly is placed in a heated autoclave, usually at

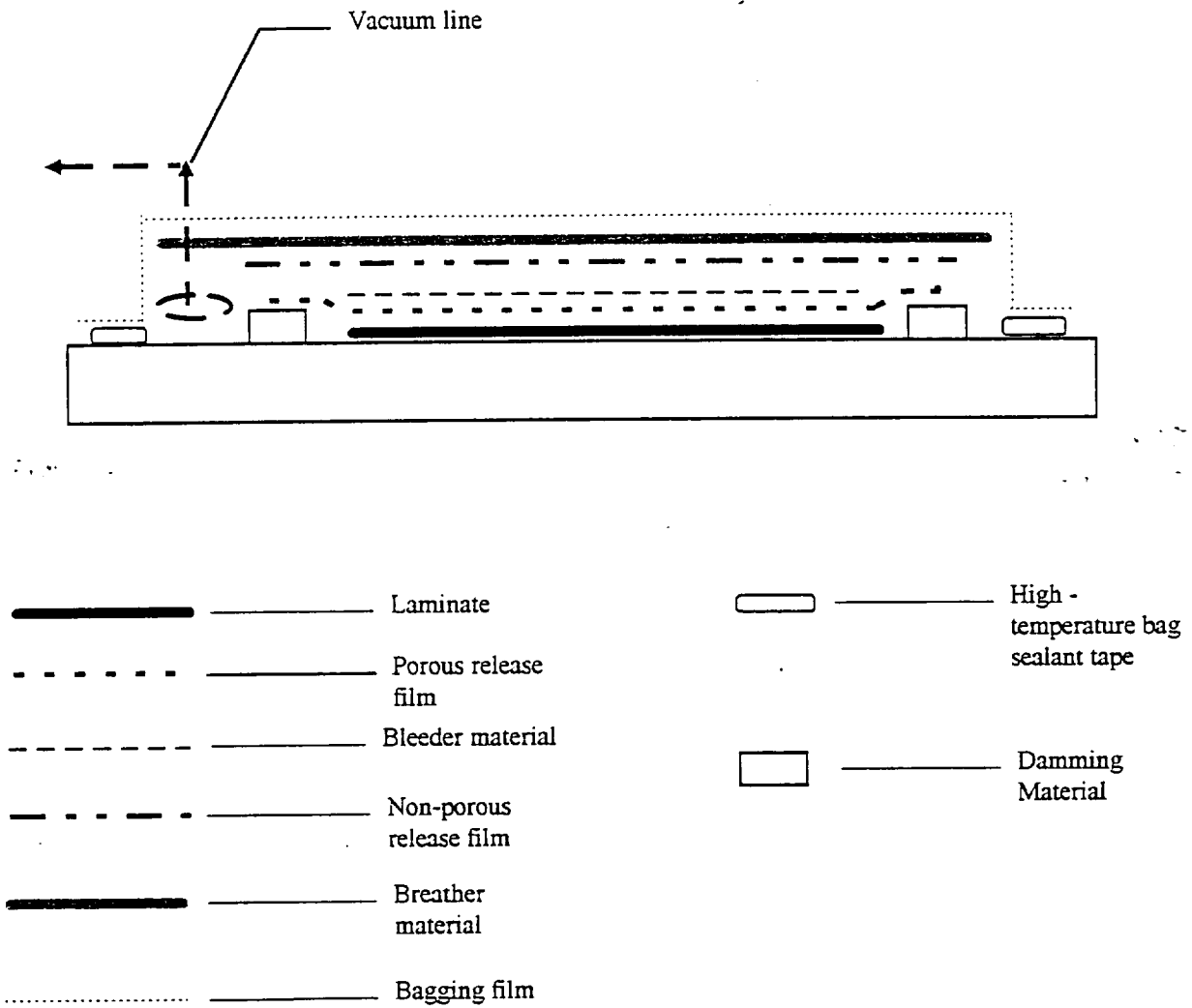
340 to 1380 kPa (50 to 200 psi). The higher pressures permit greater density and improved removal of volatiles from the resin. Costs of large autoclaves rated to pressures exceeding 1380 kPa (200 psi) are prohibitively expensive, so autoclavable polyimide resin systems that require higher pressures are not used commercially. Autoclaves can be as small as one cubic foot or large enough to engulf an entire airplane wing or fuselage section, rolled into the autoclave on a specially designed cart. Autoclaves are expensive to buy and operate, therefore resin systems with short cycle times and fast heating and cooling ramp rates are desirable.

PMR-15 and other commercially available polyimide resin systems are supplied in two distinct forms: (1) as a 'neat' resin to be matched by the end user to roving on a loom or braiding machine or to a preform (cloth or braid) of reinforcing fibers, or (2) as a 'prepreg', which is an industry expression for pre-impregnated ready-to-mold material in sheet form or ready-to-wind material in roving form. Prepreg may be either cloth, mat, unidirectional fiber, or paper impregnated with resin to be placed between layers of reinforcement. Most of the solvent has already been removed from PMR type prepregs, leaving the material slightly tacky. The supplied cloth sheets need only to be cut to shape, laid-up on tooling with the fibers in the proper orientation, then molded to the final form. Prepreg is much more popular than neat resin because the product comes ready-to-use, and the end-user does not have to worry about the correct formulation for the resin or disposing of the waste excess.



Mace (1987) recommends a debulking process for every three plies of a lay-up in a radically contoured autoclave part using polyimide resin systems. In the debulking process, the lay-up is exposed to 82 °C (180 °F) air under a vacuum of 75 kPa (22 in Hg). This requires that the lay-up be vacuum-bagged on the tool and that the entire assembly then be moved into an oven unless the tool contains its own integral heating mechanisms. Several debulking stages will be required for a thick part, and because a certain amount of heat and pressure are applied during the process, the low temperature end of the final cure cycle is affected. The first layers on the tooling will be more imidized than the outer layers. A majority of the alcohol solvent and some of the absorbed water will be removed this way.

Final preparation for the autoclave cure begins after the debulking process is completed. The low-temperature bagging material is removed, and the part is prepared for cure by applying the separator, bleeder, barrier, breather materials, and a Kapton polyimide film bag that is sealed with high-temperature bag sealant (see Figure 2.12). Roberts (1987) discusses the differences between breather and bleeder, noting that the two materials have distinct and separate functions. A breather is required to provide adequate air flow over the part and to enhance the integrity of the vacuum bag by providing padding and helping to minimize tearing of the bag, while a bleeder may be present to soak up excess resin from the laminate. When a bleeder is present, it must be separated from the breather so that the breather is not impregnated with resin during the cure cycle, which nearly always results in resin-starved parts due to removal



**Figure 2.12:** Vacuum bagging with damming technique and a bleed resin system.

of excess resin from the part. Breather is also important to provide a clear pathway for volatiles to escape from inside the confines of the bag, ensuring that the entire surface of the bag receives the same pressure from the atmosphere inside the autoclave. If the breather does not permit good airflow, local pockets of lower pressure (because the vapors are compressible, while the liquid resin is incompressible) will occur in areas in which the volatiles under the bag cannot escape. As PMR-type resins have a tendency to flow copiously at certain temperatures (termed the flow window, see next section), the bleeder system must be minimized to prevent laminate over-bleeding, which will result in a resin-starved composite. For lay-ups of up to 50 plies, one layer of fiberglass cloth is generally sufficient to ensure the release of volatiles, yet retain the proper amount of resin in the laminate of 40-45% by volume.

Vacuum is generally applied through the breather system for the entire cure cycle, while the autoclave chamber is pressurized during the period of lowest resin viscosity, 230-250 °C (446-482 °F). The reason pressure is applied in the low-viscosity range, and not before, is to fully establish the maximum fluid hydrostatic pressure, which is important to the compaction of the fibers, correct resin content establishment, and evolution of the volatile gases for transport out of the vacuum bagged tooling. The tooling must provide for the control of the resin flow during the very low viscosity condition by using the following critically important concepts, which establish the proper effective fluid hydrostatic cell for autoclave curing of laminates. First, the tool must contain the resin within the fibers of the laminate and

bleeders and not allow uncontrolled edge bleeding of the resin. Second, the tooling must allow the hydrostatic pressure of the fluid to reach its maximum. Third, complete compaction of the laminate fibers must be possible. In the event that the tool does not adequately contain the resin flow, a damming technique is employed. The dam, made of metal or high-temperature bag sealing tape, creates a barrier to resin flow next to the edge of the part, as shown in Figure 2.12 (Roberts 1987).

In the same article Roberts (1987) also describes the results of several fluid hydrostatic cell pressure experiments which were run on special tooling with two pressure transducers measuring both laminate and fluid pressure. Some of the more interesting and unexpected results are: (1) the laminate pressure never actually reached the autoclave pressure because of the pressure required to compact the fibers of the laminate, the breather and bleeder, and the bagging material; (2) the liquid resin pressure attained only about 18% of the autoclave pressure due to the fact that the compaction of the fibers limits the amount of pressure the liquid can exhibit which is a result on the limit of the size of the fluid hydrostatic cell and thereby the amount of pressure applied to the liquid; (3) the laminate pressure took much longer to build to its final pressure than did the autoclave pressure due to the requirement to compact the fibers at the onset of the pressure application; and (4) the pressure within the liquid resin reached a maximum and then levelled off, seemingly because of the chemical reaction occurring within the resin, which causes the resin to transfer much of its energy directly to the fibers and not to the liquid. These results reaffirm the need to

ensure that the fluid hydrostatic cell maintains the highest integrity during the cure cycle providing adequate fluid hydrostatic pressure to consolidate the voids and porosity in the resin, resulting in high quality laminates.

### **2.2.2 Resin Transfer Molding**

Johnson (1987) defines Resin Transfer Molding (RTM) as a closed-mold low-pressure process that allows the fabrication of composites with a wide range of complexities and sizes. The process is differentiated from other molding processes in that the dry reinforcement and the resin are combined within the mold cavity to form the composite component. The fiber reinforcement, which may be pre-shaped, is placed in the mold, which is then closed. A tube connects the closed mold cavity with a supply of liquid resin of suitable viscosity, which is pumped or transferred into the tool under low pressure, usually with the assistance of vacuum. A time and temperature dependent cure cycle is then implemented to cause the resin to 'cure', or solidify, as the mold is held closed by some form of pressure such as screws, clamps, or hydraulic force. Finally, the part is removed from the mold and any necessary finishing operations are performed.

Stark and Breitigam (1987) note that resin transfer molding has several advantages over other forms of composite parts manufacture offering potential processing, cost, and design advantages. Resin transfer molding allows relatively fast cycle times, highly reproducible part dimensions, good surface definition and appearance, good quality control, low clamping pressure, easily learned operator skills,

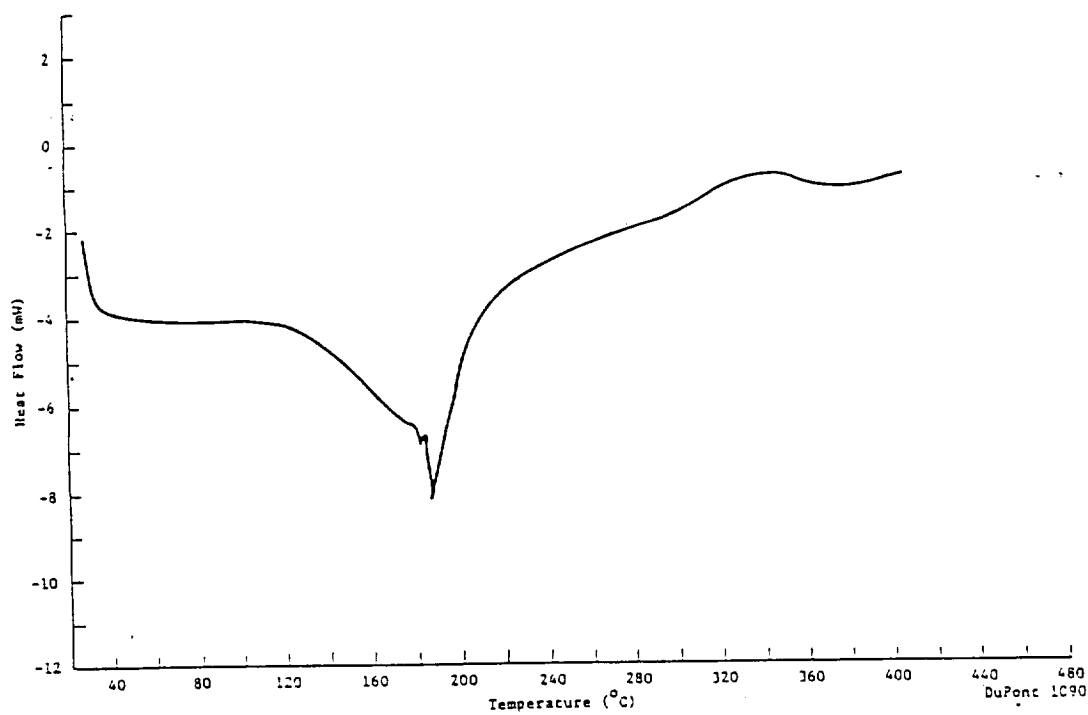
and low capital investment as opposed to other techniques, such as autoclave molding. In many cases, RTM represents the only method available for manufacturing certain geometrically complex structures and shapes, often without high-cost tooling. Large near net shapes can also be easily accommodated since RTM is not limited to the size of an autoclave. Additionally, worker exposure to hazardous chemicals in the resins can be greatly reduced compared to other methods of fabrication because the resin system is contained in the plumbing, pump or mold cavity and the worker is not directly exposed to the chemical compounds.

PMR type resins are not amenable to normal RTM because the mold is generally closed, with no path for the volatiles to follow to be removed from the enclosed mold cavity. Sadler *et al.* (1996) report that it is possible to resin transfer mold AMB-21 by using a mold which allows the solvent and condensation products to be removed through strategically located vents that open into the mold cavity. The other ends of the vents are connected to a vacuum source for the imidization and consolidation portion of the cure cycle. The work proved it was possible to evaporate the solvents and remove the condensation products of the imidization reaction without removing the impregnated preform from the mold, and consolidate the preform by pressurizing an integral steel diaphragm.

### **2.2.3 Resin Flow Properties**

Vannucci (1977) stresses that the presence of thermal transition regions account for the ability to successfully process PMR-type polyimides. Termed the "melt-flow" temperature range, the width of these regions depend on a number of

factors (including the chemical nature and stoichiometry of the monomer reactant mixture, and the prior thermal history of the PMR prepreg) and occur over a fairly broad temperature range. Differential scanning calorimetry (DSC) studies have shown the presence of four thermal transitions which occur during the overall cure of PMR-type polyimides. These four phases are illustrated in the DSC graph for a dried sample of PMR-15 resin that has not been subjected to any thermal treatment (termed "unstaged") in Figure 2.13. A change in the slope of the curve is indicative of a change in the type of reaction and delineates a thermal transition region. Note that this graph does not start at zero, the entire curve has been shifted downward by about 2mW. The sharp drop in the curve below 40 °C (104 °F) is a result of the drying of the residual solvent. The first, second, and third transitions are endothermic (with a negative heat flow below the zero on the Heat Flow axis) and are related to the following: (1) melting of the monomer reactant mixture below 100 °C (212 °F), (2) *in situ* reaction of the monomers at 140 °C (284 °F) to form prepolymers, and (3) melting of the norbornenyl terminated prepolymers at the range of 175-250 °C (347-482 °F), accompanied by a reduction in viscosity and referred to as the melt-flow temperature range. The fourth transition, which should be above the zero axis of heat flow and therefore exothermic, is centered near 340 °C (644 °F) and is related to the addition crosslinking reaction. To a large extent the excellent processing characteristics of



**Figure 2.13:** Differential Scanning Calorimetry plot for PMR-15 with no previous thermal treatment (St Clair and St. Clair, 1984).



PMR polyimides can be attributed to the presence of these widely separated and chemically distinct thermal transitions.

This viscosity change in the melt-flow temperature range is fundamental to the processing of the resin system as it allows the oligomers, with their chemically reactive end-caps, to move more or less freely in the liquid state and also allows the volatiles to nucleate and be drawn out of the resin. Studies by Wilson (1988) indicated that one critical element of the PMR curing cycle is the width of the melt flow region (flow window) of the third thermal transition region prior to the final crosslinking reaction. The characteristics of this flow window depend on both the molecular weight and molecular weight distribution of the prepolymers (Dynes *et al.*, 1984). The flow characteristics of the resin also enables the application of external pressure for proper fiber compaction and determine the final resin content of the composite part (Roberts, 1987). If the flow characteristics of the imidized oligomer can be determined during the cure cycle, particularly the third transition region, then the processing window can be accurately defined.

Polyimide formulations with even higher thermo-oxidative stability (TOS) temperatures are being sought, generally by substituting more thermally stable monomer reactants or end-caps or using formulations with higher molecular weight oligomers. Chuang *et al.* (1994) notes that when the molecular weight of the oligomeric polyimides is low (e.g.,  $n = 2,3$ , where  $n$  is the number of repeating units), such as PMR-15 ( $n = 2.087$ ) and AMB-21 ( $n = 2.0$ ), the PMR approach ensures easy

processing. While low molecular weight oligomers provide easier processing, they often do not have the higher thermo-oxidative stability and toughness exhibited by polyimides with higher molecular weights. However, as the molecular weight of the prepolymer is increased, the melting temperature and the melt viscosity also increase, severely restricting the resin flow during processing (Vannucci, 1987). The commercial success of polyimides in a variety of high-technology applications can be attributed to resin matrices with a good balance of thermo-oxidative stability, high glass transition temperature, and processing parameters (Hopper and Sauer, 1987).

## CHAPTER 3

### EXPERIMENTAL METHODOLOGY

#### 3.0 Introduction

The methods and parameters of processing the PMR-type polyimides are critical to the successful fabrication of a composite part. Times, temperatures and pressures all play a crucial role as the resin begins to dry, then polymerize and finally cross-link to form the finished component. As Gosnell (1987) observed: "When dealing with a thermosetting polymer, the process engineer must realize that the polymerization is dynamic, that both its course and the final product performance are both a function of the thermal history and environment of the living, growing molecule, and that the processing must be consistent with these factors."

This chapter will present the method used to formulate an AMB-21 resin solution of suitable viscosity for Resin Transfer Molding. A diagram of the mold will be given, as well as illustrative photographs of the mold components and assembly. The bladder used to pressurize and consolidate the preform into a fully dense structure presented many engineering and process difficulties which will be detailed and the subsequent solutions to the problems will be given. The cure cycle, from injection of the resin to removal of the composite tube from the mold, will be enumerated and a schematic of the mold plumbing will be shown. Additional sections will describe the procedures and equipment used to analyze and characterize the neat resin and evaluate the finished composite tubes.

### 3.1 Preparation of resin

AMB-21 resin is relatively easy to prepare using basic chemical lab equipment such as scales, boiling flasks, condensing columns, and a hot water bath. In addition, it is suggested that the powdered monomers be screened (sieved) to eliminate 'clinking', or the agglomeration of the powders, which will result in incomplete mixing. This section presents a complete and tested procedure for the batch formulation of approximately 750 ml, which is enough to fabricate about four or five thin-walled composite tubes of 2" diameter and 1' length with a resin volume of approximately 40 %.

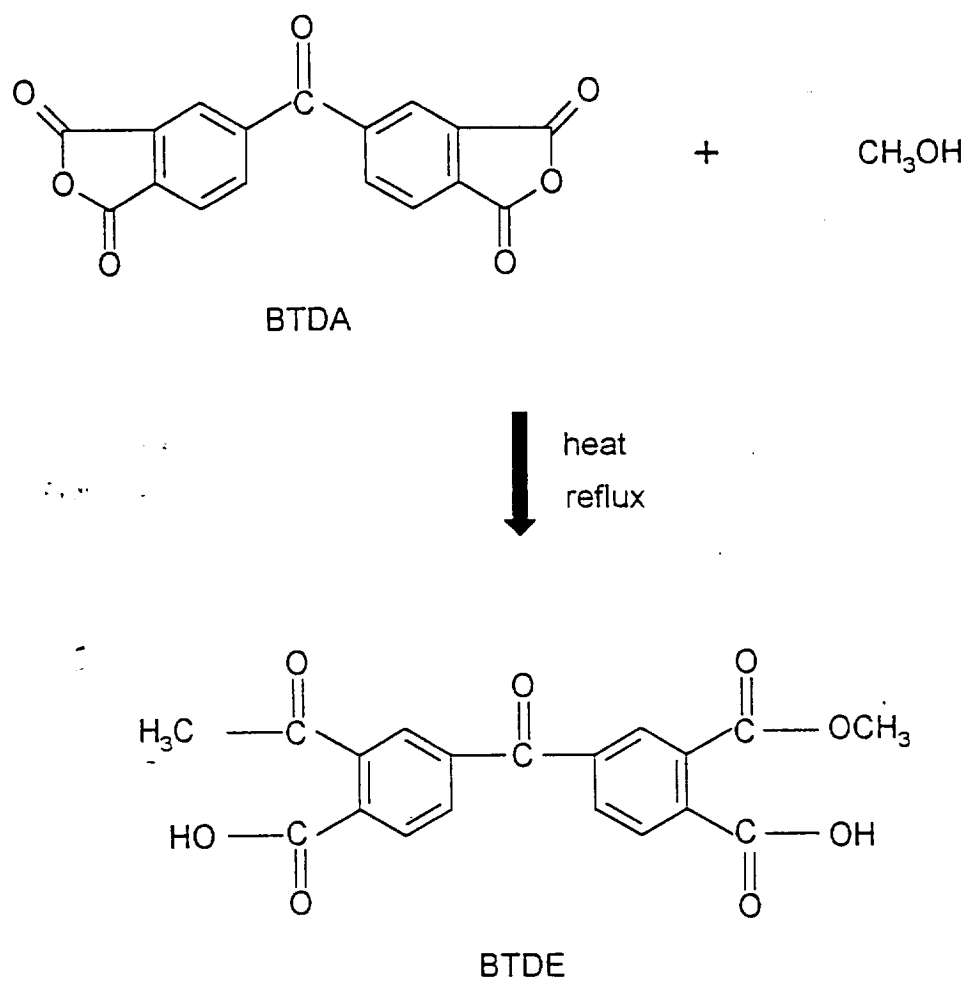
The viscosity of the resin solution will gradually increase as the short-chain oligomers begin to form during the process of imidization. The resin can be kept in a freezer for a period of two to three months with no appreciable degradation of properties. Room temperature storage is not recommended, however, as the imidization process increases the viscosity of the resin to unacceptable levels in a few weeks. The resin solution should be removed from the freezer and allowed to warm to room temperature before resin transfer molding is attempted and returned to the freezer as soon as possible after the molding is complete. If necessary, warming of the resin may be accelerated by floating the bottle containing the resin in a bucket of room temperature water. Some settling of the monomeric solids will also occur during storage, and a gentle swirling of the resin solution prior to injection is urged. Vigorous shaking is not recommended, however, as the formation of air bubbles decreases the amount of actual resin that can be pumped into the mold cavity.

AMB-21 is a blend of three monomers in an alcohol and acetone solution: 3,3',4,4'-Benzophenonetetracarboxylic Diester (BTDE), 2,2'-Bis[4-(4-Aminophenoxy)phenyl]propane (BAPP), and Bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic acid methylester, also known as Nadic acid monomethyl ester, (NE). The BAPP and NE are obtained from Chriskev Company, Inc. in Leawood, Kansas. The BTDE must be synthesized by esterifying 3,3',4,4'-Benzophenonetetracarboxylic Dianhydride (BTDA) into the corresponding diester by refluxing in methanol. The BTDA is also available from the Chriskev company. The esterification reaction is shown in Figure 3.1.

The following recipe will yield about 750 ml of AMB-21 resin with a viscosity of approximately 600 cP (at 25 °C). The molar ratio of monomers in the solution is:

2 mole BTDE	28.6 mole percent BTDE
3 mole BAPP	42.8 mole percent BAPP
2 mole NE	28.6 mole percent NE

1. Fill water bath to about one inch below upper rim with warm water, plug bath into wall socket and set heat to "high". The water temperature should be 95 °C (203 °F).
2. Zero or tare out the scales. Place 500 ml boiling flask on pan and record weight. Place plastic funnel into boiling flask and record weight.
3. Weigh 161.1 gms of BTDA into flask, add 161.1 gms methanol and swirl gently to mix.
4. Attach a reflux condenser to the boiling flask (be sure to use a small amount of stopcock grease between the two glass pieces) and then attach both pieces to a ring



**Figure 3.1:** Esterification of BTDA to BTDE.

stand using finger clamps. Place boiling flask into hot water bath and turn on the cooling water to the condenser.

5. Gently swirl the flask-condenser assembly every few minutes to dissolve the BTDA. After about thirty minutes of gentle boiling with reflux the solution will turn a clear straw yellow color. Continue to reflux for an additional two hours.
6. Remove the boiling flask from the hot water bath and allow to cool for thirty minutes with the reflux condenser attached and the cooling water running. This is now the BTDE diester solution with some excess methanol solvent.
7. During this time record the weight of a solvent-resistant bottle (glass or Nalgene™) of at least 1000 ml capacity. To this bottle add 307.9 gms BAPP (previously screened to at least 20 mesh). Add 100 gms acetone to the BAPP powder and cap the bottle, then shake vigorously to dissolve the powder into a slurry.
8. After the BDTE has cooled for thirty minutes remove the flask from the reflux condenser and re-weigh (weights should match the  $161.1 \times 2 = 322.2$  gms initial weight within one gm). Pour the BDTE into the BAPP/acetone solution, transferring as much as possible.
9. Weigh the "empty" boiling flask and add 25 gms of acetone. Swirl to dissolve as much of the BTDE as possible and again transfer the contents to the resin monomer solution.
10. Weigh "empty" boiling flask once again (weight will be different from previous weights) and add 25 gms of acetone to the flask, swirl, and transfer contents to resin

solution. This will give a total of 150 gms of acetone in the resin solution. Cap and shake the resin solution.

11. Weigh the resin solution and record weight. Add 98.1 gms of Nadic Ester (NE) which has been previously screened to at least 20 mesh. Re-cap the bottle and shake vigorously to dissolve all of the powders into the solution.
12. Place the resin solution into the rheometer water bath (set at 25 °C) overnight for temperature equilibration.

Measure and record viscosity the next day. Viscosity may be adjusted by adding more acetone for a less viscous mixture (lower value of cP) if needed.

Several small batches of resin were prepared using the methods described above. The first batch of resin (B1) was prepared initially with only 100.0 gms of acetone solvent, giving a viscosity of about 1098 cP when checked the next day. This viscosity is considered too high for transfer molding. Batch B1 was subsequently diluted with another 50.0 gms of acetone and immediately re-checked, giving a viscosity of 458 cP. It was decided to use 150.0 gms of acetone for the next batch and all subsequent batches. The viscosity of the mixture should be in the 500-700 cP range if the solution is prepared as described, depending on the amount of time between mixing the resin solution and checking the viscosity.

The resin should be stored in a freezer at 0 °F or below until needed. It will keep for at least three months if stored under these conditions, although the viscosity will slowly increase due to the formation of short chain oligomers. There is no need to store



the mixture under an inert gas blanket as the formation of the oligomers is time and temperature dependent, and the presence or absence of ambient oxygen will not effect the polymerization rate. The resin may be warmed on the benchtop or placed in a warm water (room temperature) bath prior to use. When properly prepared, the solution will have a dark, clear tea brown color shortly after mixing which will gradually change to a very dark brown clear liquid in the course of a few hours. Some small 'clinkers' or undissolved particles may also remain immediately after mixing, but these will dissolve overnight if the bottled solution is left in the water bath.

### **3.2 Resin Characterization and Thermal Analysis**

There are several accepted analytical methods used on both neat resin and fabricated composite parts that aid the process engineer in understanding the reaction chemistry of a resin and in the search for an acceptable cure cycle and increased processability for a particular resin system. This section will present a brief description of some of the more common analytical methods. Results of tests performed using these techniques on the AMB-21 resin system will be presented in a later chapter.

After making a batch of resin, rheological properties of the resin solution can be obtained relatively quickly through the use of a Brookfield viscometer, which provides a sensitive method for material characterization because flow behavior is responsive to properties such as solvent content, formulated molecular weight and molecular weight distribution. Formulation changes are readily discernible by the use of the rotating spindle

reometer, and the effects of aging on the resin can also be quickly determined. The viscosity of the resin is directly related to the processability of the fluid, and there is a rather narrow 'window' or range of acceptable viscosities. A low viscosity fluid will be easier to pump, but will contain a significantly higher percentage of solvent that must be evaporated from the mold cavity during the drying portion of the cure cycle. Conversely, a high viscosity or 'thick' resin will have a much higher solids content but will be more difficult to pump into and through the fibers in the enclosed mold cavity. Resin viscosities in the range of 500-800 cP proved to be acceptable for this particular application of resin transfer molding.

The Brookfield Viscometer measures the torque required to rotate an immersed spindle in a fluid. The spindle is driven by a synchronous motor through a calibrated spring, and the deflection of the spring is indicated by a digital display. For a given viscosity the resistance to flow, or viscous drag, is proportional to the speed of the spindle rotation and is related to the size and shape of the spindle. The drag and subsequent deflection of the spring will increase as the spindle speed and/or rotational speed increases, and this drag can be measured by a transducer and is indicated by a digital readout. It is desired to keep the 'percent torque' reading of the display as close to the maximum value of 100 as possible because the viscometer is guaranteed accurate to within  $\pm 1\%$  of the full-scale range of the spindle/speed combination in use, and this 1% tolerance of full-scale viscosity applies to all readings, representing a smaller percentage of measured viscosity as

the actual torque reading increases. In general, the accuracy of the viscosity value will increase as the percent torque reading approaches 100 (Brookfield 1988).

Thermogravimetric Analysis (TGA) measures the weight of a sample under varying conditions of temperature and pressure. Generally the test is run under a constant pressure and flow rate of an inert gas, and the temperature is raised at a constant rate. An extremely sensitive micro-balance continuously weighs the sample as the temperature is increased, and results are plotted on a graphically using axes of percent weight loss versus temperature. Analysis of the graph can yield information about the mass percent of volatiles present in an initial sample or the mass percent of volatiles evolved during a condensation reaction. Furthermore, by comparing the differing slopes of a graph, a determination can be made as to what types of reactions are occurring in different temperature ranges, for example condensation, cross-linking or thermal decomposition.

Thermomechanical Analysis (TMA) measures the changes in length or thickness of a sample as a function of temperature. The length or thickness of a small sample is determined and input to the computer program before the test is begun, and the machine monitors the change in thickness as the temperature is increased. TMA is generally used as a test for the glass transition temperature ( $T_g$ ) of a matrix material by determining the difference in the slopes of the thickness-temperature plots above and below the  $T_g$ . Below the glass transition temperature the matrix is in a crystalline rigid form while above the  $T_g$  the polymer is much more "rubbery" as bonds between some molecules are free to rotate.

Analysis is done by a computer program; the slopes and tangent lines are drawn on the

chart, and the intersection of the tangent lines determines the  $T_g$ , which is plotted and displayed. TMA can also be used to determine the coefficient of thermal expansion for a sample in a particular temperature range. TMA is a destructive test if the temperature is carried above the glass transition temperature.

Differential Scanning Calorimetry (DSC) measures the amount of energy (heat) absorbed or released by a sample as it is heated, cooled, or held at a constant (isothermal) temperature. The precise measurement of sample temperature is also made with a DSC. Normal DSC measurements use a constant rate of temperature change, while the newer high-resolution DSC machines monitor the rate of change in the amount of heat absorbed or emitted. This is done by evaluating the first derivative of the change in energy with respect to time, and when the derivative reaches a certain threshold value the rate of heating or cooling is sharply reduced, thereby increasing the resolution in the critical portions of the thermal cycle. The actual operation of either method of DSC is essentially the same: two independent furnaces (one for the sample in its pan and one for an empty reference pan) are used to raise the temperatures in two separate sample chambers. When an exothermic or endothermic change occurs in the sample material, power (energy) is applied or removed to one or both furnaces to compensate for the energy change occurring in the sample. The system is maintained in a 'thermal null' state at all times. The amount of power required to maintain the system at equilibrium is directly proportional to the energy changes occurring in the sample. The information gathered by the computer is plotted as heat flow (exo- or endothermic) versus temperature. Analysis

of the plots can yield valuable information about what is happening at different temperatures in the cure cycle by noting the changes in the slope of the cures and any characteristic "bumps". Polymer growth is an exothermic process because the increasing crystallinity is a more ordered state, while volatile evolution by trapped solvents or condensation products being released from the matrix with subsequent evaporative cooling is an endothermic process.

Infrared (IR) Spectroscopy and Fourier Transform Infrared (FT-IR) Spectroscopy both provide a quantitative, rapid "fingerprint" measurement of functional groups and specific bonds in a resin system. In these tests a small sample of resin is ground in a mortar and pestle with a larger volume of a crystal (usually KBr, potassium bromide) and pressed under 80 to 100 thousand pounds of force per square inch to fuse the resin and KBr into a crystalline pellet carrying the polymer resin. Infrared (IR) light is passed through the crystal and resin at varying frequencies, and functional groups and specific bonds absorb the energy at certain clearly defined and repeatable frequencies. Plots are generally given as percent transmittance versus wavenumber. Resin at different stages of cure can be quickly evaluated to determine if expected bonds have been formed, or to detect unfavorable bonding.

High Performance Liquid Chromatography (HPLC) provides a highly reproducible chromatographic "fingerprint" of a resin which has been dissolved in a solvent. The dissolved resin and solvent is deposited on a packed column. It is then selectively eluted using a polar-nonpolar solvent mixture of varying ratio controlled by a computer program.

The resin molecules attached to the column packing preferentially desorb from the column packing at a specific and repeatable solvent ratio and flow through the column and into a detector (either ultraviolet or refractive index). The detector converts the change in the elution stream into a millivolt signal which is recorded by the computer and plotted as a graph of voltage versus time. By adjusting flow rates, solvent ratios, sample dilution and column packing material a unique chromatogram can be determined for each resin and even each stage of resin cure, as different molecules will flow through the column at highly repeatable times (which are dependent on the program of solvent ratios).

### 3.3 The Mold Assembly

The design and construction of a mold for the fabrication of polyimide composite tubes must allow for the removal of solvents and the condensation products generated by the polymerization of the monomer units through the introduction of suitable pathways for the removal of the vapors. In this regard the mold is fundamentally different from a normal resin transfer type mold, which need only have an injection and vacuum/bleed port. In addition, a means of containing and sealing the internal bladder must also be configured, as well as the necessary pressure connection for the inflation of the bladder inside the preform. This section will present diagrams and photographs of the component parts of the mold as well as the mold assembly.

### 3.3.1 Components of the Outer Mold Assembly

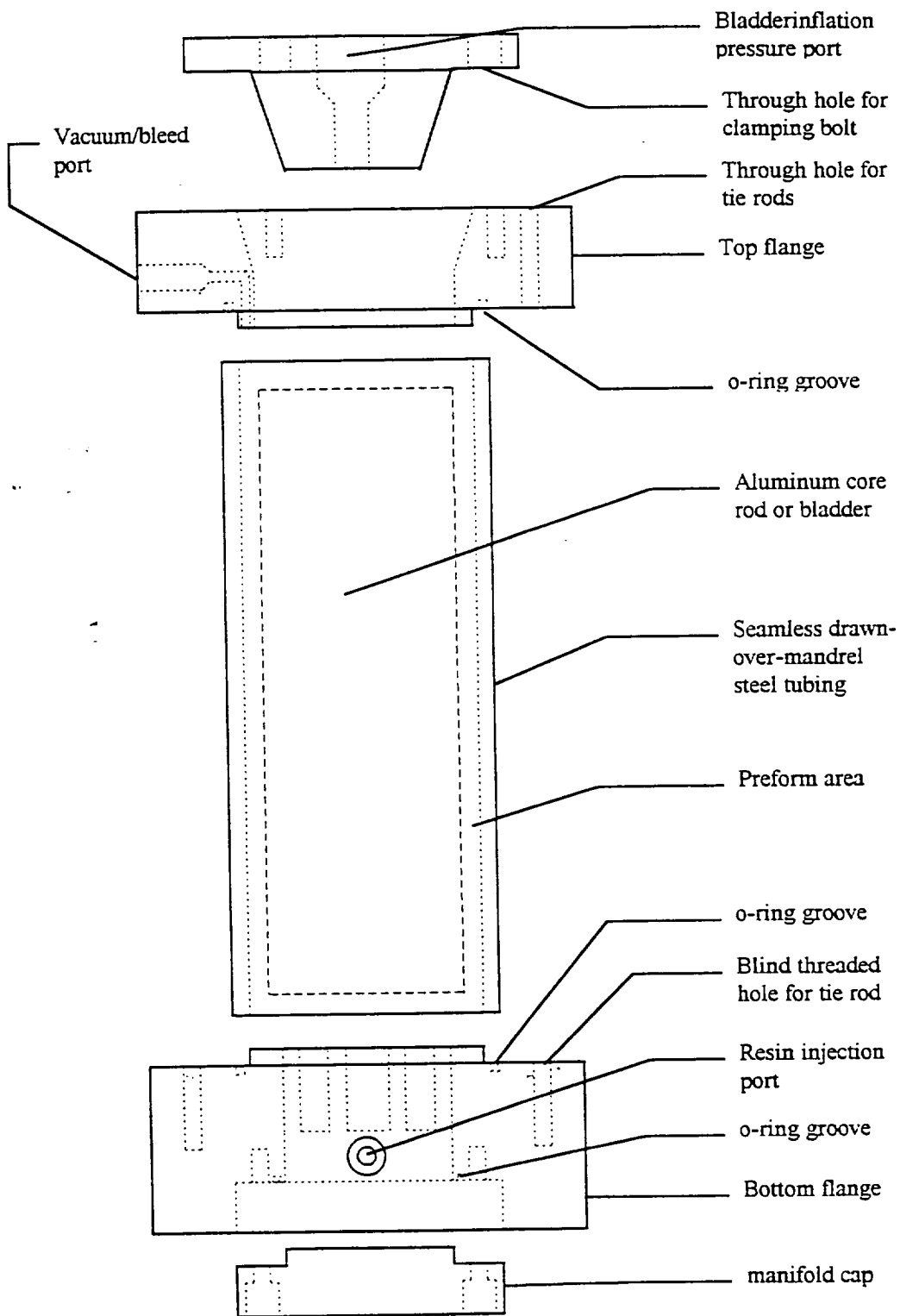
The outer mold consists of those parts of the mold that shaped the outer diameter of the finished tubular form as well as the upper and lower end caps with tie rods which hold the assembly together. The necessary fittings and piping needed to transfer the resin into the mold cavity, remove the solvents and the condensation products of the imidization reaction, and supply pressure to the bladder during the consolidation phase of the cure cycle are also considered part of the outer mold, but are so generic in nature that they will not be discussed. The outer mold was used in two distinct forms, one having a cylindrical length of seamless drawn-over-mandrel (DOM) steel tubing as the mold form, and the other of 'clamshell', or two-piece split construction, fabricated from two 26" lengths of rectangular cross-section aluminum stock which were bolted together after a 1" radius groove had been milled along the length, creating a 'bored' hole when assembled.

The upper end cap was of two-piece steel construction, consisting of a top flange and a bladder cap. The top flange served several purposes; it aligned and sealed the outer mold center section through the use of a short shoulder and o-ring groove, provided a face for the tie rods to be tightened against, provided a tapered sealing surface for the outer diameter of the bladder and location for the threaded bolt holes necessary to clamp the bladder cap, and contained a 1/4"-18 NPT threaded port through which excess resin could be bled during the resin transfer step and through which vacuum could be applied to the preform for the purpose of removing condensate products from the mold cavity during imidization. The shoulder that protruded into the mold cavity was given a generous radius

to minimize a possible high stress area upon bladder inflation. The bladder cap sealed the inside diameter of the silicone elastomer bladder by compressing the bladder between the 30° included angle tapered hole in the top flange and a corresponding taper on the bladder cap. Three holes in the bladder cap allowed threaded fasteners to supply the necessary clamping force. The bladder cap also contained a 1/4"-18 NPT threaded hole to accept a fitting for the pressurization of the bladder. Figure 3.2 shows a schematic diagram of the mold assembly while Figure 3.3 is a photograph of the major parts of the mold, showing the aluminum core and steel shim stock inside the drawn over mandrel steel pipe of the outer mold.

The lower end-cap was also of two-piece steel construction, consisting of a bottom flange and a manifold cap, and provides a reservoir manifold chamber for the introduction of resin into the mold cavity through six 5/32" holes on a 1-3/4" bolt circle drilled through the lower flange manifold area and opening into the mold cavity. A 1/4"-18 NPT port allows resin to be introduced into the manifold chamber through a 1/4" drilled hole. A shoulder and o-ring groove facilitate alignment and sealing, much like the upper flange. Three blind 1/4"-20 × 3/8" deep threaded holes in the upper surface of the flange accept the threaded rods which clamp the mold assembly together. The manifold cap is sealed to the lower flange by means of another 1/16" cross-section o-ring, and clamping force is supplied by three 1/4"-20 socket head cap screws (see Figures 3.2 and 3.3). During the solvent drying portion of the cure cycle the manifold cover is replaced with three fine stainless steel screens of 150-mesh interleaved alternately with two layers





**Figure 3.2:** Components of the Tubular mold.

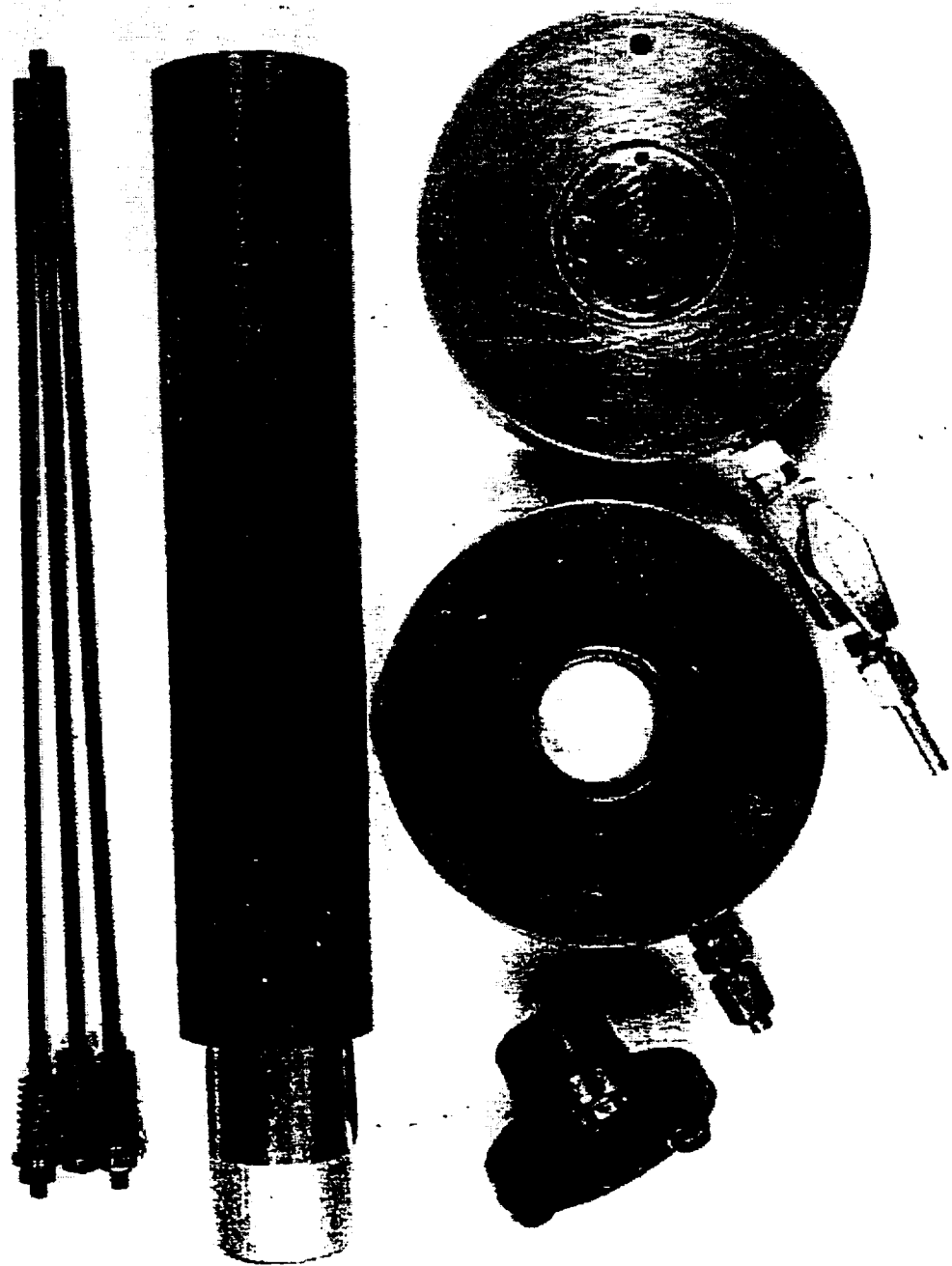


Figure 3.3: Photograph of the mold components.

of Teflon™ coated fiberglass cloth, over which a cover screen of 80-mesh stainless steel is placed to stiffen the fine screens and fabric. This arrangement allows the volatiles to escape through the screen while retaining the solid resin inside the reservoir cavity. The stainless steel screens alone will not stop the solid monomers from coming through the layers with the evaporating solvent, the Teflon™ coated fiberglass cloth must also be used.

The tie rods were also of two distinct types, necessitated by the change from a steel mold cylinder to a mold tube of aluminum construction. Standard 1/4"-20 steel threaded rod was used to secure the two flanges together when the DOM steel center section was employed. Wound steel springs or bellevue (cupped) spring steel washers were used at the top flange below the clamping nuts to maintain clamping pressure during the changing temperature parts of the cure cycle. It was found that the small threaded rods of low thermal mass gained or lost heat more rapidly than the much larger flanges and mold tube, and because of the coefficient of thermal expansion the threaded rods actually 'grew' longer at a higher rate than the rest of the mold, sometimes allowing the nuts to loosen and the clamping force to lessen, and occasionally actually losing the seal and ruining the run. When the aluminum clamshell mold tube was employed springs were placed under the nuts and three aluminum rods of 1/2" diameter, with threaded blind holes at both ends, were used because of the opposite effect: the coefficient of thermal expansion is so much greater for aluminum than steel and the aluminum absorbs heat so

fast that it was feared that the rapidly growing aluminum center section would place too great a strain on steel rods, possibly pulling them apart.

### **3.3.2 The Bladder and Related Components**

For many reasons, the expandable silicone elastomer internal bladder proved to be the most difficult aspect of the entire project. The physical requirements alone are daunting: the ability to expand and hold a pressure of 1450 kPa (210 psi) at 316 °C (600 °F) for a period of not less than two hours. When the chemical conditions of an acetone solvent and high temperature steam and methanol condensation products are also considered the task of maintaining the required pressure for any amount of time, much less long enough for the resin to fully cure, become truly formidable. The internal pressure could not be supplied by such means as differential thermal expansion between a center core of highly expanding material and an outer mold made of a material with a very low thermal expansion coefficient because of the significant volume loss due to solvent evaporation and imidization by-products. Weight loss of the resin upon the removal of the solvent, which was empirically determined to be about 22 % by weight on average for the resin prepared as described, and the losses due to condensation, which is calculated to be 12.7 %, combine to result in a 31.8 % weight loss. This means that to form a composite part with a fiber volume of 60 % and a resin volume of 40 % the weight of resin injected must be increased by approximately 50 % to make up for the losses.

Constricting pressure applied from the outside against a solid inner mandrel was also considered and ruled out because it was felt that the braided carbon fiber tubular

preform would not give the desired results in compression and would collapse unevenly, wrinkling the fabric and making the tube worthless. An expandable bladder of some type was required. The use of thin metallic deep-drawn tubes that could be stressed beyond their yield point to expand one time only, then discarded, were also considered, but again the amount of expansion required due to the loss of solvent and condensation products would have required very high pressures and a material with tremendous "stretch." For these reasons, as well as cost, an elastomeric bladder material was given first priority.

Reiss, Incorporated, (located in Blackstone, Virginia, USA) a major supplier of elastomeric products and a previous vender for NC A&T State University, was contacted and asked to supply bladder 'blanks' of 1-1/2" outer diameter, 1-1/4" inner diameter, in 10' random lengths that would be able to withstand 316 °C (600 °F) and at least 1380 kPa (200 psi). Although these conditions are extremely harsh, the supplier felt that a proprietary silicone rubber blend could be formulated to meet the requirements, and a production run of approximately fifteen lengths of tube was authorized. Upon receipt of the tubing efforts to find a suitable 'plug' for the open end of the tube inside the mold cavity, capable of withstanding the high pressure environment, were begun.

Methodology was developed for testing different configurations of end sealing which consisted of placing the silicone rubber bladder with the sealing method to be evaluated into an assembled outer mold. complete with eight layers of carbon fiber braided preform between the bladder and the outer steel tube to simulate the composite part. The mold assembly was then placed into an oven and the steel high pressure line connecting

the bladder to the pressure source was attached. The pressure was supplied by a cylinder of compressed nitrogen gas and regulated by a high pressure Air Products nitrogen regulator of 0-500 psi capability. An attempt was made to slowly pressurize the bladder at room temperature first, and if the bladder could pass a pressure test of 1450 kPa (210 psi) at room temperature then the pressure was relieved by cracking a line connection (the regulator did not have bleed-down capability). The oven was then heated to a temperature of 316 °C (600 °F) and several more pressurization and relief cycles were attempted as the mold gained temperature. No resin was injected during any of these dry runs, and the eight layers of carbon fiber preform were used to simulate the approximate thickness of the finished composite tube, thereby allowing the bladder to expand the proper amount.

Numerous attempts were made to seal the 'plug' end of the elastomeric bladder. The first was a 1-1/4" diameter brass cylinder one inch long with a 3/8" groove, 3/8" deep, turned in the outer diameter midway along the length. The silicone rubber bladder material was pushed down over the plug, then a soft (annealed) steel wire of 0.0315" diameter was wrapped twice around the bladder material in the groove area and twisted shut with pliers to seal, and then the excess wire was cut off. The wire was used because there was not enough room between the bladder and the inner wall of the steel pipe to use a hose clamp or other method of clamping such as bolted split rings. This configuration held a pressure of 1240 kPa (180 psi) before blowing out. Upon inspection of the bladder it was determined that the wire had 'cut' into the bladder material as the bladder was

pressurized, caused by the internal pressure of the bladder severely stretching the rubber in the area of the wire, which created a pinch point. The next attempt sought to relieve this pinch point by stretching another layer of bladder material about 1-1/2" long over the outside of the inner bladder to provide some padding, then wrapping the wire in the same fashion as before over the two layers. This design held a pressure of 1380 kPa (200psi) for about twenty seconds before rupturing, again at the pinch point under the wire wrap. Next, high temperature silicone room temperature vulcanizing (RTV) sealant (Permatex, Inc. product #26B) was applied to the brass plug before the rubber bladder is forced down over it, and the RTV silicone elastomer is allowed to cure for twenty-four hours before the wire is wrapped around the plug in the same manner as before. It was hoped that the RTV silicone elastomer would serve two functions: (1) seal the area above the groove so that little or no pressure could get to the area under the wire, and (2) provide padding under the bladder where the wire was creating the pinch point, relieving some of the stress. Unfortunately, the end result was the same, the bladder held the 1380 kPa (200psi) pressure at room temperature for only about thirty seconds.

At this point it was decided to try a different approach because the brass plug method was not working, and several combinations of tube folding were attempted. There are two fundamental ways of folding an elastomeric tube: the lengthwise fold made by compressing the tube flat then folding along the axial direction, and folding or rolling like a toothpaste tube. The first attempt used a lengthwise fold followed by two toothpaste tube folds, which were then secured by a hose clamp, which held pressure to 690 kPa

(100 psi) before bursting. The hose clamp created a highly stressed area where the bladder tried to expand against the sharp edge of the side of the clamp, causing it to tear. Consequently, this area was padded by an additional layer of bladder material, about 2" long, stretched over the folded bladder and placed under the hose clamp before the clamp was tightened. This configuration held the 1380 kPa (200 psi) pressure well at room temperature, lasting about twenty minutes before it was decided to try elevated temperature. At an oven temperature of approximately 205 °C (400 °F) the bladder again ruptured under the hose clamp.

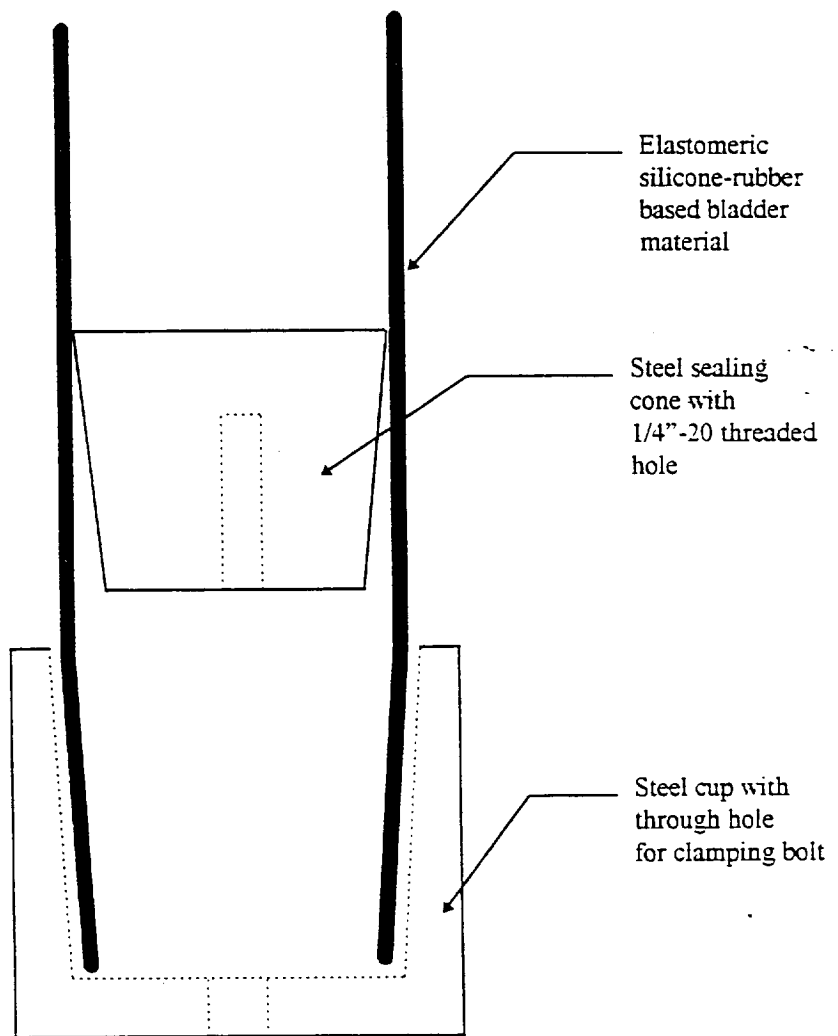
The plug method was revisited by machining an aluminum cylinder 1-1/2" in diameter, 2" long, with two shallow 3/8" grooves spaced 3/4" in from each end. The bladder material had to be stretched over the plug, causing less stress to the bladder material when the bladder was inflated. The shallow depth of the grooves were designed to lessen the stress on the bladder, and were again filled with cured high-temperature RTV elastomer sealant before the wire was wrapped around the bladder. In addition, another 2" long section of bladder was placed over the entire plug area under the wire, and the sealing wire was wrapped around the segment many times in the hope of distributing the stresses. This combination fared little better, however, as a pressure of 1100 kPa (160 psi) at room temperature caused the bladder to leak, this time not by cutting or rupturing the bladder but because of blow-by between the aluminum plug and the bladder material.

At this point a new approach was tried based on the tapered surface method similar to the manner used to seal the top flange. A cone-and-cup arrangement was



fabricated from steel and the clamping force was provided by a bolt, which when tightened pulled the tapered cone into the tapered cup, squeezing the bladder between the two surfaces and providing an excellent high pressure seal (see Figure 3.4). All edges were rounded to prevent any points of concentrated stress that could cause the bladder to rupture. This arrangement proved to be very satisfactory, able to seal during a test run with no resin present at both room temperature and at the 316 °C (600 °F) elevated temperature to pressures exceeding 1790 kPa (260 psi) for as long as four hours.

Finally it was time to attempt to mold a tube by the resin transfer molding method. The resin was injected and the cure advanced to 316 °C (600 °F), at which point a pressure of 1380 kPa (200 psi) was applied to the bladder. Surprisingly, the bladder maintained the pressure for only ten minutes before rupturing at the point where it came out from the cone-and-cup clamp. Another run yielded the same results. It was felt that the acetone solvent was degrading the silicone elastomer, so an extra layer of the bladder material was stretched over the first layer in the hope that the double thickness would not allow the solvent to contact the part of the bladder containing the pressure. The area inside the cone-and-cup remained just one layer thick, however, and two more attempts ended in the same result: the bladder ruptured just above the point where it came out of the cone-and-cup. Another attempt replaced the two-layer bladder with a fresh one layer bladder after the solvent had evaporated and the resin had partially imidized at 121 °C (250 °F) for a period of several hours. The application of pressure to the new bladder at 249 °C (480 °F) caused the bladder to rupture at just 1100 kPa (160 psi).



**Figure 3.4:** Diagram of the cone-and-cup bladder seal.

Still assuming that the acetone solvent was the cause of the bladder degradation, an aluminum core was placed in the interior of the mold cavity for the injection, drying and imidization steps, replacing the bladder, which was not necessary at these times. The round aluminum cylinder would also serve another purpose; it would ensure that the resin would infiltrate the preform evenly, and that the preform would remain concentric. The pressure of the resin during injection could move the preform if the carbon fibers were not confined, and the elastomeric bladder could bend and buckle, resulting in the possibility of a preform with an egg-shaped inner diameter. This aluminum core was 1-3/4" in diameter, the same diameter as the outside of the sealing cup, with the length cut to completely fill the mold cavity minus just enough clearance on the ends to allow the end caps to be attached. The core was coated with mold release agent to enable it to be cleanly removed from the preform after the solvent had dried and the resin had been allowed to partially imidize at 150 °C (300 °F) for one and one-half hours. After this step of partial imidization, the mold was removed from the oven and allowed to cool enough to handle, at which point the mold was to be disassembled and the aluminum core removed and replaced with a bladder and seal assembly.

The first attempt at this method proved that refinements to the technique were needed, as the dried preform, now a 'pre-preg', came out with the aluminum core instead of remaining in the steel outer mold. For the next attempt, a piece of thin steel shim stock 0.0015" thick was wrapped around the aluminum core inside the preform. The shim stock was cut as long as the core and 6-1/2" wide, just wide enough to form a slight overlap at

full expansion of the bladder. Both the shim stock and the core were coated with mold release agent. The shim stock would serve several purposes; it would allow the core to be withdrawn more easily from the prepreg, help protect the bladder from any remaining solvent, protect the bladder from physical damage due to sharp corners that may be created as the matrix imidized and hardened, provide a smooth surface to the inner wall of the completed tube, and prevent the bladder material from 'oozing' into the inner wall of the composite part, forming a mechanical interlock which may be difficult to remove and which would leave bladder material attached to the inner wall of the completed composite part. This modification to the procedure proved very satisfactory, enabling the aluminum core to be easily removed and the bladder to be inserted without harming the pre-form, so all subsequent runs employed steel shim of varying thickness wrapped inside the pre-form.

The bladder itself, however, continued to be a problem, again bursting on the next attempt even with the aluminum core and the steel shim stock. A phone call to Reiss, Inc. provided some insight into the nature of the problem. During a conversation with the chemist in charge of the formulation for the silicone rubber it was discovered that the acetone present in the solvent was not the primary cause of the degradation of the bladder. Initial conversations concerning the formulation of the bladder had not adequately explained the nature of the condensation reaction occurring during the imidization step of the cure cycle, which evolves both water and methanol. The water comes off as a vapor at the temperatures where the imidization occurs, that is to say, steam. Steam is very

degrading to the silicone rubber, causing the long chain molecules of the material to 'unzip', or come apart, thereby affecting the strength and elasticity of the compound.

Although this degradation could not be completely avoided, it could be minimized by allowing the imidization reaction to proceed further with the aluminum core inside the pre-preg instead of the bladder. This could be accomplished by leaving the aluminum core in until the resin had reached 205 °C (400 °F) or more instead of 150 °C (300 °F), giving more time for the evolved steam to be removed before the bladder was placed in contact with the resin. It was also decided that two or more layers of braided fiberglass preform (Atkins and Pierce, Inc. product 'Silasox' GM2.00) could be placed around the elastomeric bladder, providing a pathway for the removal of the steam and other volatiles while still allowing the bladder to expand. The fiberglass braided preform also served as a bleeder, or resin sponge, to soak up any excess resin squeezed out of the fibers during the consolidation step of the cycle. Additionally, a vacuum source connected to both ends of the mold assembly was employed to remove the condensation by-products more effectively during the run up to 400 °F. A thin steel 'containment ring' (1-3/4" outside diameter, 1/16" wall thickness, 0.200" tall) was also placed atop the bladder between the upper flange and the tapered cap to prevent the bladder from oozing or creeping out from between the two pieces when pressure was applied, as had been a problem on several of the earlier attempts. Conversations with Vannucci (1996) revealed that the 316 °C (600 °F) two hour final step of the cure cycle could be modified to a four hour or more phase at a lower temperature of 287 °C (550 °F), with equivalent results to the matrix but

much less stress on the bladder. These modifications proved fruitful, and several good tubes were fabricated by these methods.

Several process engineering problems remained, however. The thickness of the layer of shim stock was varied between 0.0015" and 0.006" in an attempt to find the optimum thickness. The thinner pieces of steel shim stock, such as 0.0015", 0.002", and 0.003" proved to be just too thin and flexible, resulting in several sections of crinkling or wrinkled fabric in otherwise good tubes. Figure 3.5 is a photograph of a section of tube T-10 showing a section of 'crinkled' matrix on the interior wall of the tube. There are several possible explanations for these irregularities, but it is believed that the application of the full amount of pressure, 1380 kPa (200 psi), all at once at the onset of the flow window, about 249 °C (480 °F), caused the bladder to 'lock' the two ends of the composite part in place. The 'puffing', mentioned in chapter two, caused by the escape of volatiles in the center of the tube, farthest from either vent at the ends of the tube, kept the shim stock expanded back against the bladder. When the puffing finally subsided and the bladder expanded out to its maximum, there was an excess amount of steel shim in the center of the tube, and the ends of the tube were already locked in place. The steel shim had no way to smooth itself out and remain flat, so it had to crinkle. Later attempts used a pressurize and release method from 204 °C (400 °F) to 249 °C (480 °F), as well as a thicker piece of shim stock such as 0.004", 0.005", and 0.006" with very good results. These thicker shims do leave a definite 'parting line' down the length of the tube at the point of overlap, and the wall thickness of the composite part does change sharply at this point, but it is felt that the otherwise smooth inner wall and protection of the bladder by



Figure 3.5: Photograph of tube T-10 interior showing "crinkle" zone.

the shim stock are well worth the price of a parting line. The photograph in Figure 3.6 shows a bladder assembly ready to be inserted into a partially imidized pre-preg for the final stages of the cure cycle on the left. A used piece of shim stock with the fiberglass breather inside is shown in the middle, while the two pieces of a used bladder assembly are displayed on the right.

Removal of the completed composite part from the drawn-over-mandrel (DOM) steel pipe also presented quite a challenge, especially on the longer tubes. Because of the thin wall of the composite part, there is very little to push against when it becomes time to remove the tube from the DOM pipe. Close fitting brass and aluminum cylinders, just a few thousandths of an inch smaller than the inner diameter of the steel tube, were used with a hydraulic press to force the composite part out of the DOM outer mold. Even with such a close fit the outer layer of carbon fibers often got wedged between the plug and the DOM tube wall, locking the part into place. The forty-five degree braid angle of the carbon fiber preform presented another problem. When force was applied against one end of the composite part the fibers tended to bulge out, locking the part ever tighter as more pressure was applied. The concept is analogous to pushing together a short section of braided rope held closely between two hands; the rope tends to bulge outward in the center of the length. It was possible to remove all of the composite tubes from the shorter lengths of the DOM pipe, that is, lengths less than 1', although on some occasions the steel DOM had to be thermally expanded by heating to over 205 °C (400 °F) before the composite part could be pressed out. When longer length composite tubes were



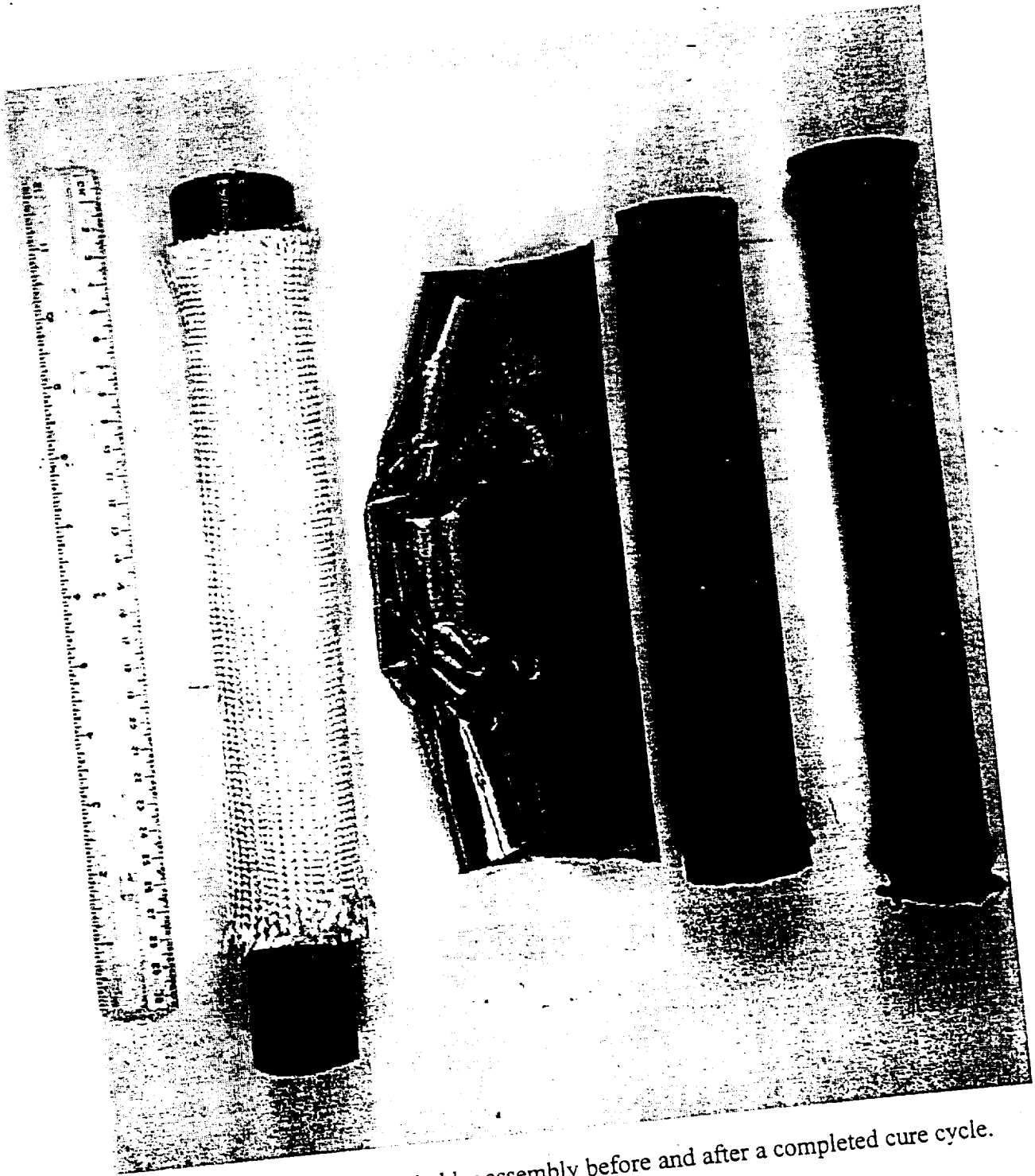


Figure 3.6: Photograph of bladder assembly before and after a completed cure cycle.

attempted, however, no amount of persuasion could push the composite part from the inside of the DOM steel pipe. It became necessary to physically cut the steel pipe off of the tube by the use of an end mill and vertical milling machine, saving the composite part but obviously ruining the DOM pipe. Unless a method can be devised to remove the composite parts by pulling them from the seamless mold tube, instead of pushing, it seems that longer length composite tubes must be fashioned in a clamshell design two piece mold assembly.

The shim stock, fiberglass breather cloth and the bladder must be removed from the completed part after the cure cycle is completed, and this proved to be an arduous task on several tubes, particularly the longer tubes removed from the clamshell mold. It became necessary to use a long, flat steel bar,  $1/8" \times 1/2"$  and 36" long, to pry the shim stock away from the inner wall of the finished part. This was a difficult and lengthy chore on the longer tubes, requiring as much as forty-five minutes to completely remove all the inner mold components. The pry bar had to be driven or pushed into the space between the shim and the composite part, then twisted to break the bond between the two. This process had to be repeated until the steel shim was completely separated from the composite tube, at which point the bladder, fiberglass braiding and crumpled steel shim could be removed with pliers. Sometimes it was easier to remove the bladder and fiberglass before beginning to work on the steel shim by using a long steel rod and hammer to drive the bladder out.

The alignment of the fibers in the braids determines the strength of the finished part because graphite fibers only have strength in the direction parallel to the fibers. If the braided preforms are indiscriminately handled or poorly aligned the finished part will not have the fibers in the proper orientation and may not perform the functions it was designed to. Because only the outer layer of braid is visible through the matrix, it is impossible to determine if the interior layers of carbon fiber are in the proper orientation except by destructive testing. It is extremely important that each layer of preform be handled with care to prevent breaking fibers, and once oriented in the proper alignment the bundle should be pulled tight and securely fastening to prevent the braid from shifting as it is pulled into the mold.

### **3.4 Resin Transfer Molding**

While the previous sections detailed the difficulties encountered in the attempts to manufacture a tubular specimen of an AMB-21/graphite fiber composite part, this section will present a thorough set of instructions for the resin transfer injection of a seamless tubular mold or a split clamshell-style mold, followed by instructions for the most successful curing cycle. The cycle is complicated, but any deletions or alterations of the described process will more than likely produce inferior parts. The entire cycle, from preform preparation to start of the final high temperature portion of the cure, can be accomplished within a period of less than eight hours. An additional four hours at the elevated temperature of 287 °C (550 °F) are necessary to fully form the part. The entire

mold assembly can then be left in the oven to cool overnight, and the part removed the next morning. Step-by-step instructions follow:

1. Assemble all mold components:

1. clamshell mold with bolts or drawn over mandrel steel tubing 2" ID.
2. aluminum rod 1.750" diameter approximately 3/16" shorter than outer mold (for the 26" aluminum clamshell mold the rod is 25-13/16" long with radiused ends)
3. steel shim stock at least 0.006" thick and 6-1/2" wide, length to match aluminum rod above
4. bottom flange with internal resin manifold area for injection and venting of resin
5. manifold cover with three 1/4-20 x 1/2" socket head cap screws
6. (3) 150 mesh stainless steel screens. (1) 80 mesh stainless steel screen, (2) Teflon™ coated fiberglass release cloths, aluminum clamping ring (diameter and bolt circle pattern to match manifold cover above), and (3) 1/4-20 x 3/8" socket head cap screws
7. top flange with integral tapered hole for bladder
8. tapered plug for top flange (to capture end of bladder), with pressure inlet fitting, three 1/4"-20 x 1" hex head bolts with washers, and (1) 3/8"-16 x 1-1/2" socket head cap screw to plug inlet fitting during injection and initial drying stages
9. bladder containment ring 0.200" tall, 2-1/16" outer diameter by 2-3/16" inner diameter
10. cup-and-cone bladder plug for 'bottom' end of bladder, with draw bolt and washers
11. tie rods with necessary bolts or nuts, washers and/or springs.

2. Coat all mold components with mold release interface and dry or bake as directed. Frekote 700NC, (obtained from Rudolph Brothers and Company in Canal Winchester, Ohio), was used on several runs with the drawn over mandrel steel tube mold but yielded inconsistent results. One mold had to be cut off of the cured tube

inside using an end mill to cut along the length of the pipe on two sides. Airtech #50, (available from Airtech International, was used in the clamshell mold with mixed results. Although the composite part released easily, some polyimide 'flash' stuck to the mold at the ends of the part and had to be scraped out of the mold with a knife. If the clamshell mold is being used, place a small amount of high temperature RTV sealant (Permatex Hi-temp RTV silicone gasket maker part #26B) along both edges of the length of the tube mold before securing the two halves of the mold together with bolts. The sealant will help prevent vacuum leaks. Since the clamshell mold is aluminum and the bolts are steel, do not tighten the bolts over 20 ft-lb<sub>f</sub> since the different coefficients of thermal expansion may cause the threads to "pull out" of the aluminum. Wipe any excess sealant from the interior of the mold and allow the sealant to cure overnight.

3. Wrap the shim stock tightly around the aluminum rod along the length. The shim stock may be pre-rolled along the length into a tight curl before the release agent is applied, this will enable the braided preform to slide over the shim stock more easily.
4. Using a helper, slide a layer of braided preform over the aluminum rod and the rolled shim stock, keeping the shim tightly wrapped and the braided preform straight on the rod. Insert a small rope with several knots tied in one end or a long thin metal wire with several washers secured to one end of the wire (to aid in pulling the bundle through the mold) and tape the leading end of the preform tightly together with the knotted rope or wired washers inside the closure, then pull the sealed end back snugly

against the rod. Carefully compress the preform against the rod and shim and work the tightness back toward the trailing end, *keeping the braids straight*. Handle the graphite fibers as little as possible to prevent breaking of the fibers. Tape the trailing end 'pigtail' tightly up against the rod and cut the braided preform past the tape. Repeat with three more layers of braid to give a total of four layers. The braid being used is Gammasox GM 2.00 braid furnished by Adkins and Pearce, consisting of 6K tows of AS4 commercial grade carbon fiber with an epoxy sizing applied during the braiding operation. Use the rope (or wire) pull the bundle carefully into the mold, keeping the braid straight, until the aluminum rod is centered lengthwise in the mold. Trim the ends of the carbon fiber braids off slightly below the mating surface of the outer mold using sharp shears or a razor knife. Discard excess braid, but retain pull rope or wire with washers for next run.

5. Place an o-ring into the groove around reservoir area of the bottom end cap and secure manifold cover with three cap screws. Wrap two layers of Teflon™ tape around the pipe threads of the injection ball valve and screw the valve into the bottom end cap securely, with the valve handle in a convenient position (upward), as previously shown in Figure 3.3.
6. Place the bottom end cap on a secure table (with the manifold cover down) and insert an o-ring into the groove in the top surface of the cap. Turn the mold outer tube assembly containing the preform and aluminum cylinder eye vertical and carefully set it onto the protruding shoulder. Place another o-ring in the bottom surface of the top

end cap and set the cap into the outer mold, checking to be sure that the o-rings on the top and bottom cap do not become dislocated. Secure the top and bottom end caps to the mold with the tie rods and the necessary bolts or nuts, washers, and/or springs.

7. Cut a one inch length of bladder and place into the tapered opening on the top end cap.

Wrap several layers of Teflon™ tape around the threads of the 3/8-16 × 1-1/2" socket head cap screw and use this bolt to seal the inlet pressure port (which is not needed at this time) in the tapered top flange by inserting and tightening the bolt into the port. The tapered top flange is now inserted into the short piece of bladder and tightened down evenly until it is snug.

8. Wrap several layers of Teflon™ tape around the 1/4" NPT threads of a right angle fitting (the other end of which is 3/8" flare fitting) then screw the right angle fitting "finger-tight" into the bleed/vent port on the outer diameter of the top end cap with the opening pointing up. Force a length of 1/4" ID clear Tygon™ hose over the fitting and connect the other end of the hose to a vacuum trap placed in-line before the vacuum pump. Close the injection valve on the bottom end cap and turn on the vacuum pump. When the gauge in the vacuum line reads at least 27 in Hg (with zero being atmospheric pressure), close the valve between the gauge and the pump, isolating the gauge with the mold for a check of the integrity of the vacuum. The vacuum should remain constant for at least fifteen minutes.

9. During this time of vacuum check, attach a short section of Norprene™ 7/16" outside diameter by 1/4" inside diameter with 3/32" wall thickness (or other suitable) tubing to the outside of the bottom inlet valve with a hose clamp, thread the tubing through the peristaltic pump, then attach the end of the tubing to a small funnel placed higher than the top of the mold. When the vacuum check has been successfully completed, fill the funnel with resin and open the inlet fill valve, making sure the peristaltic pump head is open and dis-engaged. The resin will slowly be drawn into the tubing and then begin to fill the mold. When the resin level drops into the funnel neck close the inlet fill valve and refill the funnel with more resin and repeat the process. Depending on the size of the funnel and on the temperature and age of the resin (both of which affect the viscosity of the resin) two complete funnel fulls can be drawn into the mold and perhaps a third one can be started. When the rate of filling slows appreciably, start the peristaltic pump (Masterflex 'Easy Load' model 7518-02) at a slow speed (0.5-0.7) and close the pump head. Refill the funnel as needed. A small cover for the funnel should be fashioned out of some aluminum foil (nothing fancy, it will be discarded) to keep the resin from "skinning" over, as the acetone in the resin quickly evaporates.
10. As the mold fills the reading on the vacuum gauge will show a decrease in vacuum, quickly at first to a reading of about 25 in Hg then more slowly, eventually falling to the 18-20 in Hg range (depending on the length of the mold). After three to five funnels full of the resin have been drawn and pumped into the mold some resin will be



seen at the clear outlet bleed/vent Tygon™ tube. Break the vacuum connection at the trap and continue to pump resin until one to two inches of resin rises into the vent/bleed line. Quickly disconnect the Tygon™ tubing and then attach a 3/8" straight copper riser tube (one end of which has been previously flared) that is three to four inches taller than the mold is long in a vertically upward direction. Continue to pump resin into the mold for an additional two to three minutes or until the funnel and lines are empty, then close the inlet valve. Loosen the hose clamp on the inlet valve and remove the tubing and clamp.

11. Place a small piece of Teflon™ coated fiberglass cloth about one inch square over the top of the copper tube, then cover the cloth with a small section of 150 mesh stainless steel screen followed by a small piece of 80 mesh stainless steel screen. Secure the cloth and screen to the tube with a small hose clamp. The cloth is available from National Aerospace (San Clemente, CA) as 300-3 Porous Teflon™ Coated Glass Cloth release fabric and described as a 1080 style fiberglass cloth coated with approximately 45% by weight TFE Teflon™ coating. The cloth is approximately 0.003" thick with a 500 °F maximum use temperature and controlled porosity. It is non-migrating, non-sticking, and dimensionally stable.
12. A helper may be needed to flip the mold "upside-down" (manifold chamber up) while at the same time tightening the right angle fitting to swing the copper riser tube 180 degrees so that the riser tube screened opening remains vertically upward. Remove the manifold cover bolts and use an Allen "key" in one of the bolt holes to gently pop

the cover up and off. Wipe any resin stuck to the manifold cover back into the reservoir area. Make sure that the reservoir o-ring is still in its groove. The stainless steel screens and Teflon™ covered fiberglass cloth are now placed over the opening in the following order:

- (1) 150 mesh stainless steel screen
- (1) Teflon™ coated fiberglass breather cloth
- (1) 150 mesh stainless steel screen
- (1) Teflon™ coated fiberglass breather cloth
- (1) 150 mesh stainless steel screen
- (1) 80 mesh stainless steel screen

An open-centered aluminum ring is then placed on top of the screens and secured with three 1/4"-20 × 3/8" socket head cap screws.

13. Place the mold into the oven with the screened end up. Using soft steel wire, secure the assembly to the sides of the oven or to the oven rack to prevent the mold from falling over. Place thermocouples at the center of the outside of the mold tube and at one end cap, then insulate the thermocouples with fiberglass batting to ensure that the thermocouples are reading the mold temperature and not the ambient oven air temperature.
14. Close oven doors and start strip chart recorder. Turn on the oven and adjust set point to 250 °F.
15. After one-and-one-half hours the thermocouples should indicate a temperature very close to 250 °F. Turn off the oven and open the doors. Remove the three bolts securing the screens to the manifold cavity, then remove the aluminum ring, the screens, and the cloth. The resin in the manifold cavity should be dry, and slightly

bowed upward. After checking to make sure that the o-ring is still in place replace the manifold cover and secure with the three 1/4"-20 x 1/2" socket head cap screws. Unscrew the inlet fill valve, and use a 1/4" drill bit to clear the port. Use a twisting motion to "drill" out the dried resin for about three inches, then blow the threads clean. Wrap two layers of Teflon™ tape around the 1/4" NPT end of a straight fitting (the other end is 1/4" flare) and tighten the fitting into the threaded port. Use only steel flared line inside the furnace and for at least one foot outside the furnace to connect to a vacuum cold trap and vacuum pump outside the furnace. Note that at this time the copper riser tube (with screens) is still attached. Turn on the vacuum pump and induce a vacuum on the system.

16. Close the oven doors, turn the oven back on with the same set point of 250 °F. Continue to heat for an additional one to one-and-one-quarter hours.
17. Turn off the oven and open the doors. Turn off the vacuum pump or close the valve between the pump and the mold. Remove the copper riser tube and the right angle fitting. Again use the 1/4" drill bit to clean out the port, then attach another straight 1/4" NPT fitting (with two layers of Teflon™ tape) into the port. The other end of the fitting is again 1/4" flare, and a length of steel flared tubing is connected in a 'y' or 't' arrangement so that both top and bottom flared fittings are connected to the vacuum.
18. Close the oven doors and turn on the oven. Raise the set point to 550 °F. Restart the vacuum pump and open the valve between the pump and the mold.

19. While the oven is coming up to temperature the bladder can be prepared. The following measurements are based on a 26" clamshell mold, other lengths of mold outer tube have been used and measurements of the bladder assemblies required for these tubes follow a similar pattern. First, chamfer the inside diameter of one end of the bladder to ease insertion into the sealing cup. This is done by placing a long length of bladder material into a steel pipe with an inner diameter matching the outer diameter of the bladder material (1.50"). Next, a steel surgical blade in a holder is held at an angle and the pipe is rolled or turned, cutting the inner diameter of the bladder material more than the outer diameter, resulting in a chamfered cut. The bladder material is then drawn through the steel pipe until 26-1/8" is exposed, and the surgical blade is again used to cut the material, this time at a right angle, by piercing the bladder material with the point of the blade and then working the blade around the edge of the steel pipe, producing a clean cut. Another 25-5/8" of bladder material are withdrawn from the steel pipe and cut off for use as a second layer of elastomeric material, providing some cushioning effect for the inner bladder as well as filling the void between the 1-1/2" outside diameter of the inner bladder and the 1-3/4" inside diameter of the steel shim so the inner bladder does not have to expand as much. The longer length of bladder material is sealed with a cone-and-cup type arrangement as follows: a nut and washer is screwed onto a long length of 1/4"-20 threaded rod (at least four inches) and then the cup is placed on the threaded rod, after which the cone is screwed down tight on the rod. At least 1" of threaded rod should be exposed.

between the cup and the cone. A mark is placed 1" back from the chamfered end of the bladder material and the bladder is pushed over the cone and into the cup up to the mark. A wrench is used to tighten the cone into the cup as tight as possible, then the threaded rod is placed in a vise and the excess rod is cut off with a hack saw and the burr removed with a file. To double layer the bladder, the free end of the bladder material is folded longitudinally and secured with a short section of soft steel wire. A 3' length of steel or aluminum welding filler rod is inserted into the folded area around the steel wire and bent back to form a loop, which is then twisted shut and secured. The 25-5/8" section of bladder material is placed around the filler rod and the free end of the welding filler rod is clamped in a vise. The second layer of bladder material is worked over the first until the second layer is seated against the steel cup, at which point the steel wire securing the other end is cut off. To expand the first bladder inside the outer layer a three foot steel pipe of 1-1/2" OD is forced into the inner bladder using a slight positive air pressure introduced through a rubber stopper sealing one end of the steel pipe, then withdrawn. Two pieces of fiberglass braided material (Adkins and Pearce SM 2.00) of stretched length 28" and 29" are then placed over the outer layer of bladder material (shorter length under the longer length) to introduce a pathway to the ends of the mold for any condensation products and act as a bleeder.

20. When the thermocouple readings indicate that the outer mold and cap temperatures have reached 410-425 °F (about one hour), turn off the oven and open the doors.

The prepreg is now partially imidized, or partially 'B-staged'. Remove the thermocouple connections to the mold. Untwist the steel securing wires and save for the next part of the cure cycle. Turn off the vacuum pump (or close the valve between the pump and the mold) and disconnect the flared fittings at the mold, using a wrench on the NPT fittings screwed into the mold to keep them from loosening instead. Remove the mold from the oven and dis-assemble the end caps from the central mold tube. Also remove the flanged and tapered top pressure inlet port from the top end cap, discarding the one inch of bladder material used to seal the two pieces. The 3/8"-16 x 1-1/4" bolt must also be removed, and replaced with a 1/4" NPT by 1/4" flare right angle fitting (the NPT end should be wrapped with two layers of Teflon™ tape).

21. Using a hydraulic press or a similar device, remove the central aluminum core rod, leaving the steel shim stock (the purpose of the shim stock is to facilitate removal of the rod, as well as creating a smooth inner wall of the composite tube when the bladder expands). On the longer molds it may be necessary to start the core rod moving with the press and then clamp the mold in a vise and carefully "persuade" the core rod out of the mold using a hammer and solid drift long enough to push the core rod completely out, such as a wooden "broom handle."
22. The bladder assembly may now be pushed into the space vacated by the aluminum core, being careful that the outer layers of fiberglass braid do not become tangled and

- stuck inside the mold. It may be helpful to tape the fiberglass braid to the rubber bladder with masking tape to get the braid inside the mold, then remove the tape.
23. The end caps are re-attached to the mold tube with the fittings pointed in the same direction as before using *new* o-rings. If the aluminum clamshell style mold is being used high temperature RTV sealant (Permatex #26B) should be spread around the sealing area and new o-rings. The top end cap must be placed over the bladder assembly after any excess fiberglass braid has been folded or jammed back below the sealing face. The tie rods are then re-tightened.
24. At this point the flanged pressure inlet top cap must be sealed. Some problems were experienced with the 200 psi pressure "oozing" the bladder material out the top of the mold, but the introduction of a thin "containment ring" negated this problem. Place the containment ring on top of the end cap, over the bladder and inside the bolt circle for the flanged and tapered top sealing cap. Then secure the top pressure inlet with the three 1/4"-20 x 1" bolts and washers tightly down on the containment ring with the previously attached right angle flare fitting pointing in the same general direction as the other fittings.
25. Place the mold back into the oven with the pressure inlet up (manifold chamber down) and secure the mold assembly to the sides of the oven with the steel wires. Re-attach vacuum lines and thermocouples (with insulation batting cover). Attach pressure line (must be steel line with flared fittings). Pressure is supplied by bottled high pressure nitrogen gas through a two-stage regulator followed by a back pressure regulator set

- for a maximum pressure of 210 psi. Pressure is monitored by a large scale pressure gauge and a transducer which supplies between 0-6 volts to the strip chart recorder. Close the oven doors and turn the oven on, with a set point of 650 °F. Check that the bladder can withstand the required pressure of 210 psi by adjusting the regulators to feed 210 psi to the bladder then closing the valve between the bottle and the rest of the system (the bladder and the pressure gauge) and monitoring for a drop in pressure for 2-3 minutes, then relieve the pressure. Re-start the vacuum pump and check for vacuum leaks, then continue with vacuum for the rest of the cure cycle.
26. When the thermocouples indicate that the mold has reached 400 °F raise the internal bladder pressure to 200 psi and bleed off several times ("bump" the pressure). This "bumping" procedure should be carried out until the mold temperature reaches 470 °F, at which point the pressure should be left at 200 psi for the rest of the cure cycle.
  27. When thermocouples indicate that the mold has reached a temperature of 470 °F (averaged between the outer mold wall and the end cap) lower the set point to 480 °F and hold for thirty minutes. Pressure should be at 200+ psi.
  28. After thirty minutes at 480 °F raise the set point to 550 °F and leave overnight with the pressure and vacuum applied.
  29. The following morning turn off the oven, vacuum and pressure and allow the mold to cool in the oven to about 300 °F (this will ease the tension in the tie rods). The mold can then be removed from the oven and dis-assembled, at which time the composite tube can be removed.



30. The bladder assembly must now be removed from the mold, as well as the steel shim.

Screwdrivers or a long flat rod may be used to loosen the shim from the inner wall of the composite tube, then the shim stock can be removed with pliers by twisting it out.

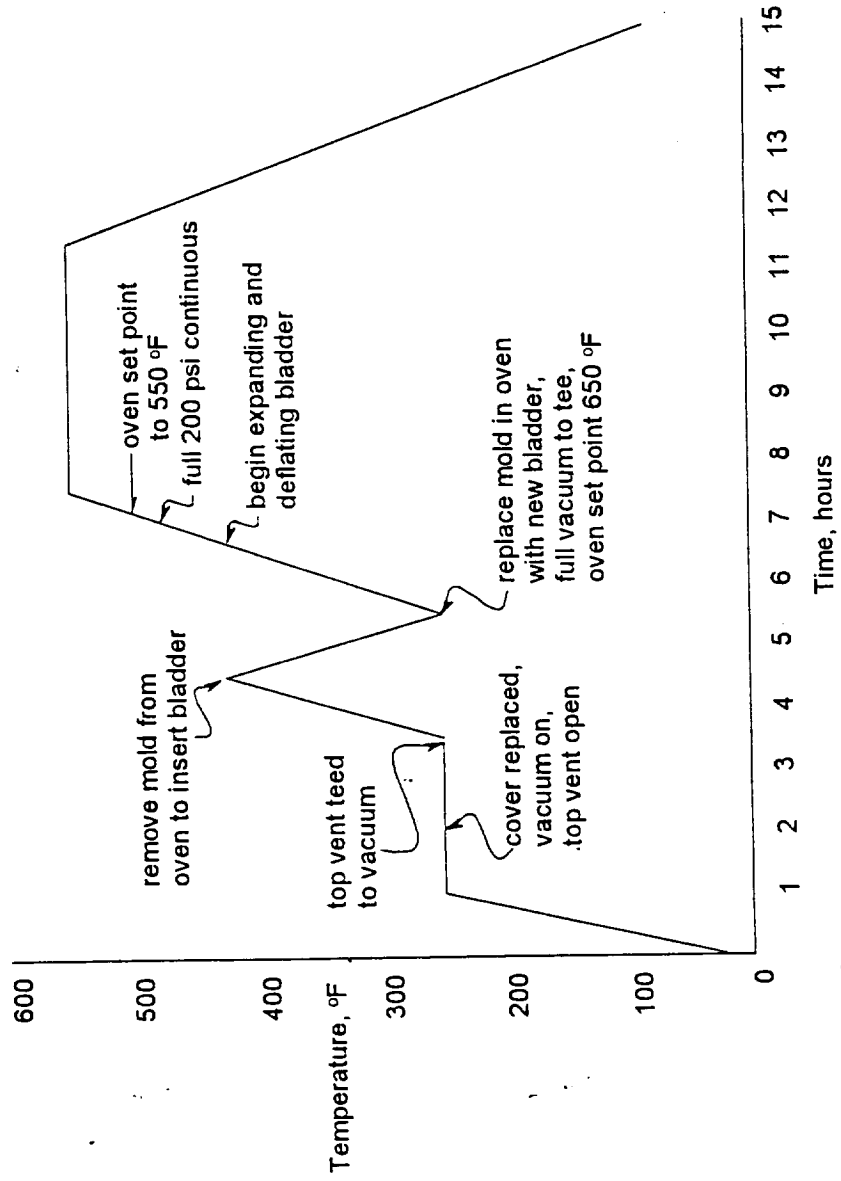
Figure 3.7 illustrates the cure cycle developed for the tubular form molds using modified resin transfer molding techniques to introduce the resin into the closed mold cavity, which has been previously loaded with the graphite fiber preform. Figure 3.8 is a schematic diagram of the thermocouple connections and the vacuum and pressure plumbing for the consolidation phase of the cure cycle.

A total of nine thin-walled composite tubes of acceptable quality were fabricated using the AMB-21 resin solution and modified resin transfer molding techniques. The flash from the rough ends of each tube was cut off and discarded. The physical dimensions and characteristics of the resultant tubes are presented as Table 3.1. Some comments about the physical appearance and/or problems encountered with the fabrication of individual tubes are given below:

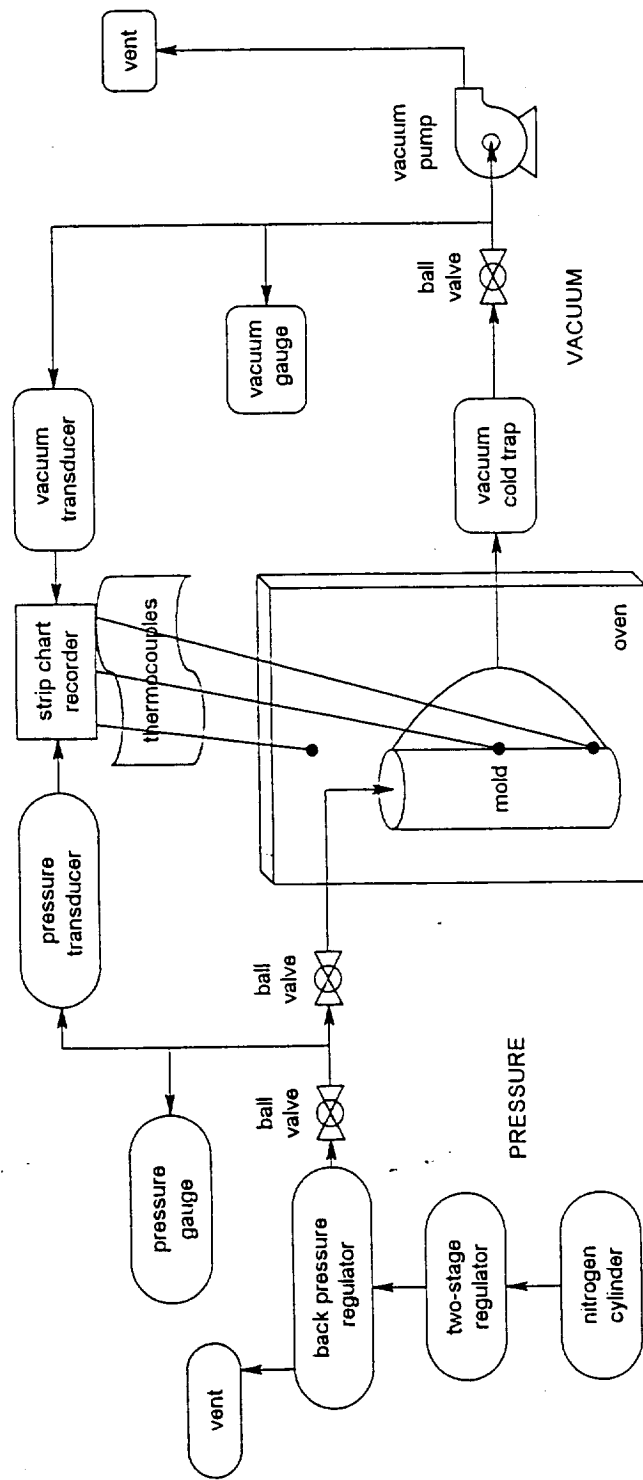
T-8: Inner diameter of tube wall is not smooth because tube wall 'crinkled' when pressure was applied, probably due to incomplete imidization and subsequent 'puffing' of resin. Outer diameter of tube showed slight visible porosity.

T-9: Inner diameter smooth for entire length of tube. Three small areas where resin did not completely flow and infiltrate fibers on outer diameter, fibers look 'dry'.

T-10: Steel shim stock 'crinkled' on inner diameter. Some visible porosity.



**Figure 3.7:** AMB-21 resin transfer molding cure cycle for tubular mold.



**Figure 3.8:** Schematic of mold plumbing and thermocouple connections.

**Table 3.1:** Fabrication data and physical characteristics of composite tube forms.

Tube #	Date	Resin Batch	Shim Thickness (in)	Outer Diameter (in)	Wall Thickness (in)	Length (in)	Weight (gms)
T-8	06/24/96	B4	0.0015	1.995 - 1.999	0.056 - 0.077	7.9	72.76
T-9	06/27/96	B4	0.003				
T-10	07/09/96	B4	0.002	1.995 - 2.000	0.057 - 0.091	8.2	82.90
T-11	07/11/96	B4	0.005	1.994 - 2.000	0.058 - 0.066	7.7	67.22
T-12	07/16/96	B4	0.004	1.997 - 1.998	0.059 - 0.066	6.6	
T-13	07/18/96	B5	0.004	1.997 - 1.998	0.071 - 0.084	3.4	
T-14	07/23/96	B4	0.004	1.996 - 2.000	0.062 - 0.069	8.5	79.62
T-15 A	07/30/96	B5	0.004	2.020 - 2.033	0.058 - 0.069	8.1	75.18
T-15 B	07/30/96	B5	0.004	2.019 - 2.031	0.064 - 0.069	8.1	79.01
T-15 C	07/30/96	B5	0.004	2.018 - 2.030	0.056 - 0.069	9.0	86.05
T-16	08/08/96	B5	0.006				

T-11: Very good tube, slight visible porosity. Visible seam line on inner diameter from shim stock. Some areas of poor flow and incomplete infiltration where matrix does not completely cover fibers, region looks 'dry'.

T-12: 'Crinkle' in middle of length of tube. One-half of tube used for  $T_g$  determinations, other half used for showpiece.

T-13: Mold had to be cut from around composite using end mill. Tube was good at both ends, center of tube has more visible porosity. Collapsed area along length at the seam line where shim stock 'crinkled' along length and bladder could not fully expand. Because of collapsed section this tube was cut into several shorter lengths for display.

T-14: Outer layer of braid is not completely straight around tube. Several 'dry' looking small spots on inside of tube. Some porosity visible along outer diameter, especially towards center of the length of the part.

T-15: First attempt using the clamshell (two piece) outer mold. Very easy to remove composite tube from mold after fabrication. Two sections of 'crinkling' which divide the tube into roughly three equal lengths. Visible porosity is significantly higher in the middle one-third of the tube. Steel shim stock becomes very difficult to remove from a tube of this length, as it is bonded to the inner diameter of the composite tube.

T-16: Second run with the clamshell mold. Tube is to be used for display purposes.

Photomicrographs of a section of Tube T-11 at 50, 100 and 400 power magnification are shown as Figures 3.9, 3.10, and 3.11, respectively. The white circular "dots" are the carbon fibers, the gray area between the dots is the polyimide matrix, and the irregularly shaped black patches are areas of voids. All of the photographs are taken viewing a section along the length of the tube, generally referred to as the axial, longitudinal, or "z" direction.

### 3.5 Post-curing of Tubes

Free-standing postcures in an air-circulating oven are used to increase the glass transition temperature of the completed component. This section will describe the treatment of samples sent to NASA for a post cure cycle.

One small four inch long tubular sample from fabricated Tube T-12 and several small 1/8" square pieces from the same tube were sent to NASA Lewis Research Center in Cleveland, Ohio for determination of glass transition temperatures before and after a post cure cycle. The short section of fabricated tube was also carefully dried and weighed before and after the post cure cycle in order to determine the percent weight loss due to the thermal treatment. The tube was placed in a vacuum oven and heated to about 100 °C (212 °F) while the oven is evacuated to at most one-half atmospheric pressure. After four hours at temperature the oven is turned off and the part is allowed to cool under vacuum. When the part returns to room temperature after cooling overnight it is carefully weighed.



Figure 3.9: Photograph of Tube T-11, 50 power magnification, axial view.

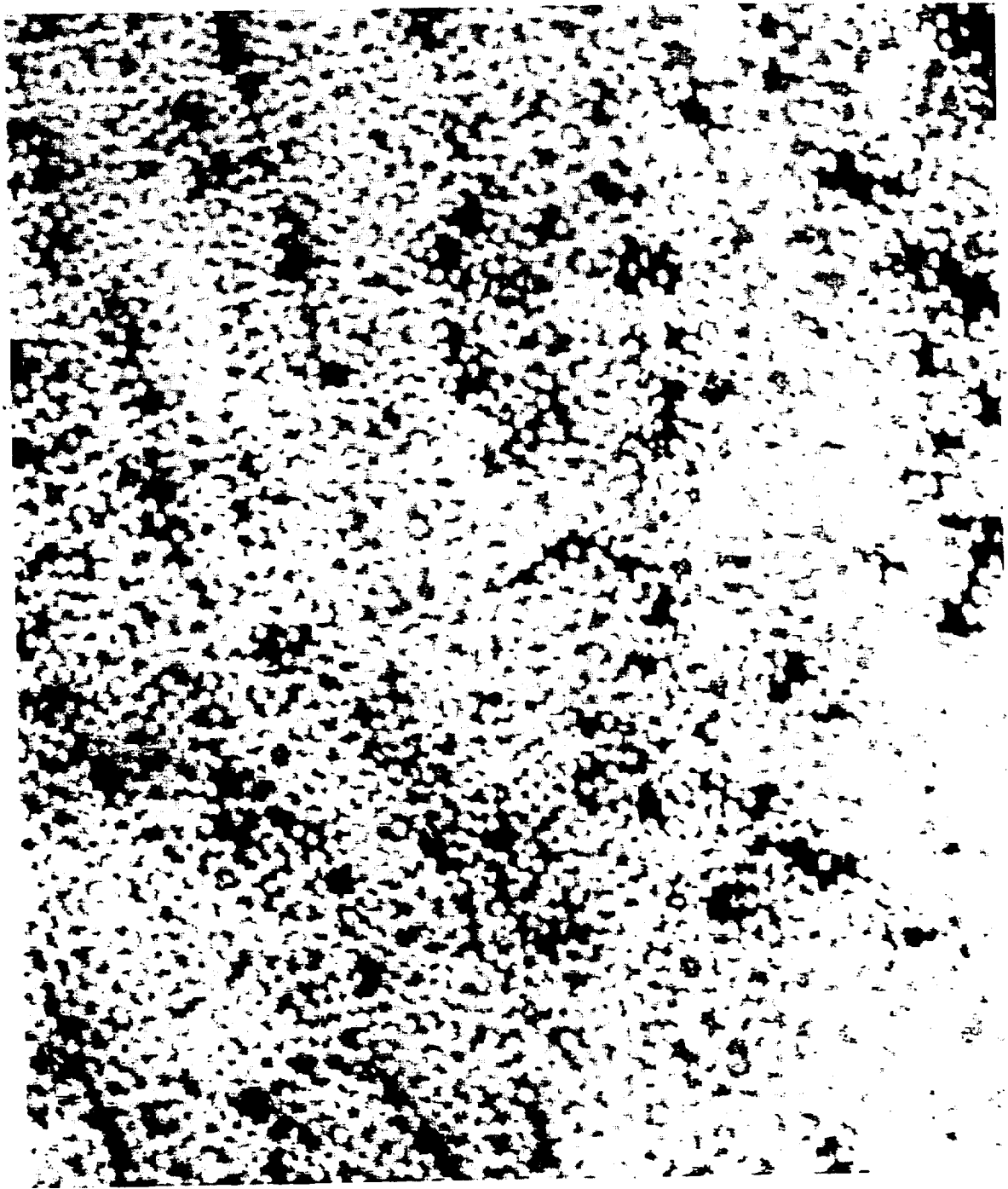


Figure 3.10: Photograph of Tube T-11, 100 power magnification, axial view.



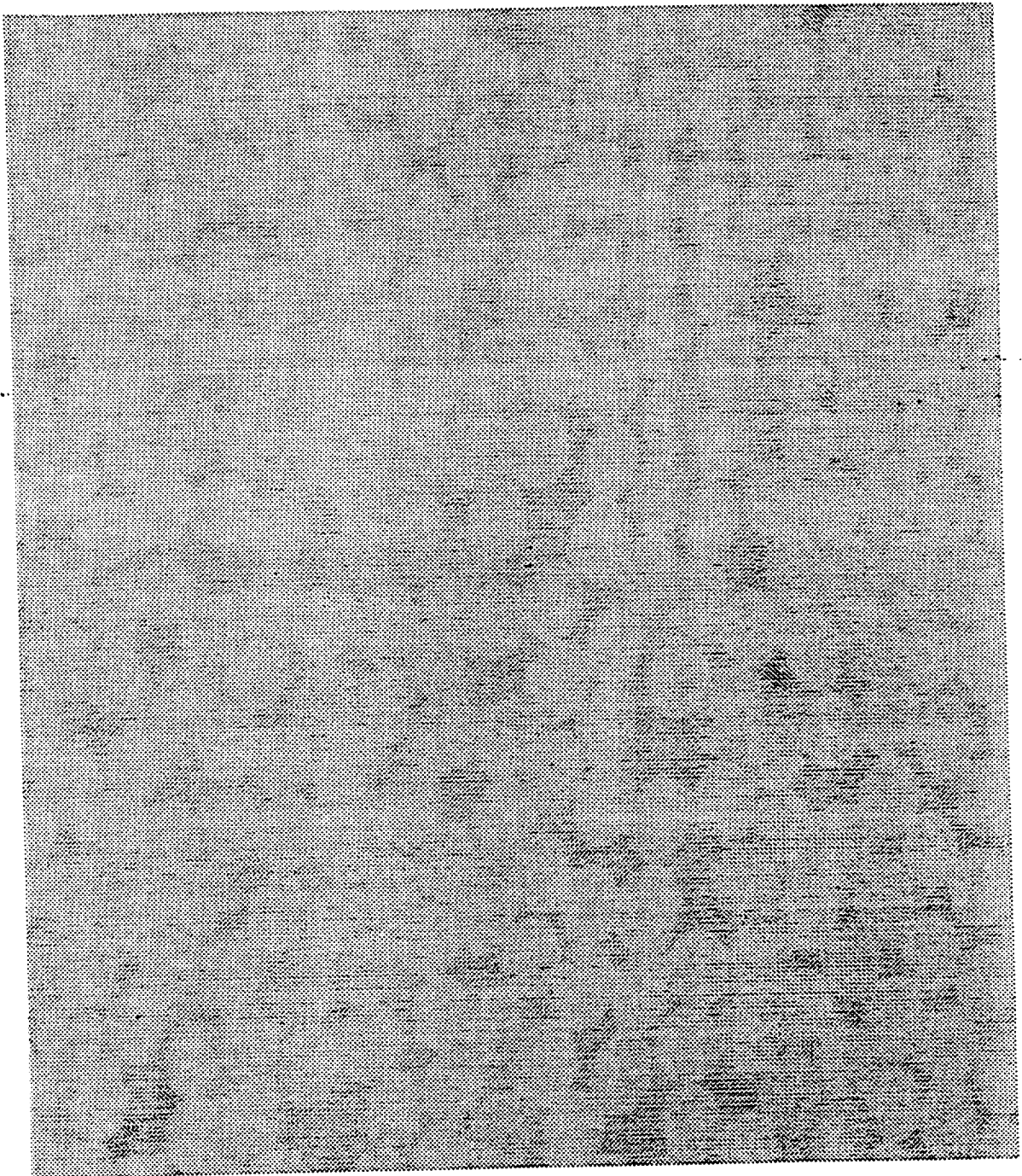


Figure 3.11: Photograph of Tube T-11, 400 power magnification, axial view.

This procedure is followed before and after the post cure cycle to determine the percent weight loss due to the cycle.

The one-eighth inch square pieces were used to determine the glass transition temperature before the post cure treatment by thermomechanical analysis (TMA). After the weight for the percent weight loss is determined at the end of the post cure cycle a small piece is cut from the tube and the glass transition temperature for this piece is determined by TMA. The difference in the glass transition temperatures between the two samples is due to the thermal treatment of the post cure cycle.

The post cure cycle was:

- room temperature to 500 °F at 10 °F/minute
- hold at 500 °F for 2 hours
- 500 to 550 °F at 1 °F/minute
- hold at 550 °F for 2 hours
- 550 to 600 °F at 1 °F/minute
- hold at 600 °F for 4 hours
- 600 to 625 °F at 1 °F/minute
- hold at 625 °F for 8 hours.

The part was then allowed to cool in the closed oven until the internal temperature of the oven reached 200 °F or below.

### 3.6 Specific Gravity

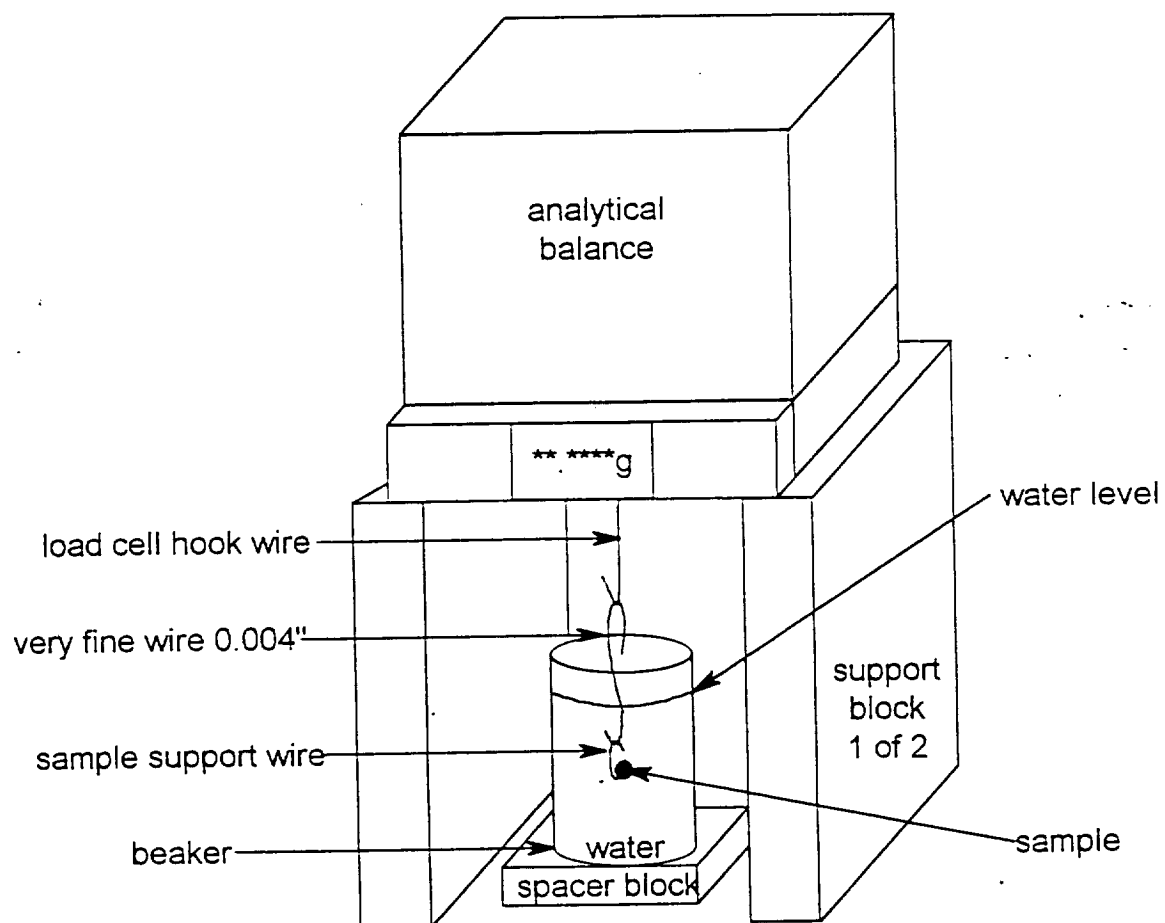
Specific gravity is a useful analytical tool for making quick and accurate judgements about the differences in porosity or degree of uniformity between composite samples. Specific gravity is defined as the ratio of the density of a substance to the density

of a reference substance. For an impermeable solid the specific gravity is the ratio of the density of the solid at a specified temperature to that of water at 4 °C, taken as 1.0, because at 4 °C water is the most dense and at this temperature one cubic centimeter (or one milliliter) of water weighs exactly one gram by convention. Specific gravity can be related to density by a simple multiplier, which factors in the discrepancy caused by taking specific gravity measurements at room temperature while density is defined at 4 °C (this multiplier is 0.9975 for tests made using water at a temperature of 23 °C). Generally, the most convenient method for determining specific gravity is by Archimedes method, which consists of weighing the sample in air and under water, then calculating the specific gravity by a simple equation. This section will describe a standardized method for the determination of the specific gravity and density of carbon fiber composite samples.

ASTM standard D 792-66 *Standard Methods of Test for Specific Gravity and Density of Plastics by Displacement* (Storer 1993) details the procedure for determining the weights of the composite sample in air and water. This procedure was carried out on entire eight to ten inch long composite tubes and on sections or samples cut from tubes after mechanical testing. First, the sample was weighed on an analytical balance with an accuracy of 0.1 mg, this weight is recorded as "a". A piece of 1/16" stainless steel welding filler rod wire with hooks formed in both ends was suspended below the pan (on a hook attached to the load cell) before this measurement and the scale is 'tared out' to ignore this additional weight. A length of very fine wire with loops in both ends, Awg wire gauge number 36 (0.004") or finer, was hung below the wire attached to the pan or

load cell. The water level of the immersion vessel falls somewhere along this length of very fine wire, and because of the small size of the wire and the subsequent minute amount of water that the wire displaces the degree of immersion is not a factor in the calculations. If this very fine wire is not used then the degree of immersion must be maintained at the same level for all measurements, necessitating the addition or removal of water for each specimen (see Figure 3.12).

Another length of stainless steel filler rod wire was bent to form a hook at one end and a loop or spring clip type arrangement at the other end. This piece of wire actually holds the specimen and hangs completely immersed in the water below the very fine wire. The weight "w", which is the apparent weight of the very fine wire partially immersed and the heavier sample clip wire totally immersed in water, can now be obtained by filling a 600 ml glass beaker or other suitable container with water at 23 °C and immersing the wires until about one-half of the very fine wire is under water, then recording the weight. The sample clip wire was then removed from the loop of very fine wire and the sample was placed into the heavier wire loop and clipped by spring tension, then replaced in the water. At this point it is very important to remove any and all air bubbles which may be attached to the surface of the sample or the wire, as these bubbles will lower the apparent weight of the sample. The use of a fine wire to dislodge the bubbles is recommended. The weight "b", which is the apparent weight of the specimen and the sample wire completely immersed and the very fine wire partially immersed, can now be recorded. The



**Figure 3.12:** Diagram of set-up for determining specific gravity.

calculation for the specific gravity of the sample at 23 °C in water at 23 °C, denoted Sp gr

23/23 °C, is:

$$\frac{a}{(a + w - b)}$$

As previously noted, the density at 23 °C can be determined by multiplying this number by 0.9975.

### 3.7 Fiber Volume Testing

Fiber volume testing determines the amount of fibers present in a resin-matrix composite sample by dissolving the resin portion of a weighed composite specimen in a heated digestion medium. The residue, consisting solely of carbon fibers, is filtered, washed, dried, and weighed. The weight percent of fiber can then be converted to a volume percent if the fiber and composite densities are known. The void content due to entrained air or entrapped volatiles of a composite sample can be determined if the specific gravity and the fiber volume of the sample are known. There is an established direct correlation between porosity and mechanical properties, particularly matrix dominated properties such as interlaminar shear strength and transverse flexural strength. This section will detail the procedure used for the acid digestion of sections of the composite tubes made with AMB-21 resin. Because of the resistance of polyimides to chemical attack from most substances, rather extreme conditions are required to digest AMB-21: hot concentrated sulfuric acid followed by oxidation with 50% hydrogen peroxide. The

matrix cannot be just burned off, as with fiberglass-reinforced composites, because the carbon fibers would oxidize also.

ASTM D3171-76, the *Standard Test Method for Fiber Content of Resin-Matrix Composites by Matrix Digestion, Procedure B* (Storer 1993) for polyimides, was used as the basis for this digestion procedure, with some slight modifications. Several samples were cut from each composite tube using a silicone carbide grit edge hack saw blade or a silicone carbide grit edge hole saw of 1-1/8" diameter. The resulting edges were sanded smooth before the specific gravity and density measurements. The weight of the thoroughly dried composite specimens, which is the same as the dry weight used in the previous specific gravity test, is recorded as "a". At this point clean, bone-dry Gooch coarse-fritted glass crucibles used to catch the carbon fibers after the digestion were marked, weighed and the weights recorded. The specimens were then placed in small beakers (100-200 ml capacity), and concentrated sulfuric acid was poured over the samples until the samples were completely covered. A watch glass was placed on top of the beakers, and the samples were heated in a hot water bath or on top of a hot plate until the acid turned dark and fuming. A glass rod was used to stir the acid/sample mixtures, thereby exposing fresh acid to the samples. The beakers were then removed from the water bath and allowed to cool, then small quantities of 50% hydrogen peroxide were gradually added to oxidise the organic matrix material, which turned the solution clear once again. Great care must be exercised at this point as this is a violent, highly exothermic reaction. The oxidation must be done under a fume hood, and the front shield

should be pulled down as far as possible. Long rubber or latex protective gloves should be worn to protect the hands and arms of the technician. Safety glasses must be worn.

The spent acid/oxidiser solution was poured through a coarse frit Gooch type crucible (using vacuum filtration) to capture any stray carbon fibers that were accidentally poured out of the digestion vessel. A vacuum cold trap was used in line before the vacuum pump to condense any vapors present which could have been detrimental to the pump. The acid/oxidiser procedure was repeated until the densified and consolidated composite sample was completely digested, leaving the graphite fibers looking like shiny black hairs with no lumps of solidified resin, and fresh acid no longer turned dark following several minutes of exposure to the sample at elevated temperatures.

The digested specimen was thoroughly rinsed with many changes of water until the pH of the water rinse was about 6, each time pouring the rinsate through the same Gooch fritted glass crucible (under vacuum filtration) to catch any and all stray carbon fibers. To aid in drying the fibers, acetone was poured in the beaker completely covering the fibers, the glass rod was used to mix and stir the fibers for several seconds, then this rinsate was poured through the Gooch fritted glass funnels, this time transferring all of the carbon fibers from the beakers as well. The empty beakers were rinsed with another acetone wash and this was also poured through the filter to make sure that all of the fibers had been captured. Finally, Gooch crucibles with the fibers were removed from the filter funnels and wiped clean to remove any dissolved rubber from the sealing ring between the crucible and the funnel, then placed in an oven at 100 °C (212 °F) overnight to remove



residual water and acetone. The filters and fibers were allowed to cool to room temperature in a dessicator then weighed on an analytical balance. The weight of the fibers, "W", was determined by subtracting the weight of the filter from the weight of the filter and fibers.

The weight percent fiber in the composite can be calculated by:

$$\text{Fiber, weight\%} = \left( \frac{W}{a} \right) \times 100$$

The volume percent fiber in the composite can be calculated by:

$$\text{Fiber, volume\%} = \left[ \frac{(W/F)}{(a/c)} \right] \times 100$$

where:  $W$  = dry weight of fiber in the composite

$a$  = dry weight of the initial composite specimen

$F$  = fiber density (1.82 for AS4 fibers), and

$c$  = composite density.

In order to determine if the digestion medium has had any effect on the graphite fibers it was necessary to attempt to digest a weighed piece of dry fabric in the same conditions as the composite samples for the same amount of time. If the graphite fibers did not lose any weight upon subsequent drying then no adjustments need to be made to the weight of the fibers, 'W' above. If, however, the digestion medium does decrease the weight of the carbon fibers upon exposure to the digestion cycle, then the weight 'W' must be increased in the same proportion to give a corrected fiber volume.

### 3.8 Determination of Void Content

Voids are essentially inclusions of air or trapped gasses from the imidization reaction that have not escaped from the resin and are cured into the finished composite part. Voids are detrimental to the part because they cannot transmit structural stresses and the presence of voids allows for the uptake of atmospheric water which can decrease the thermo-oxidative stability of the part. A void content of less than one percent is considered acceptable for most properly cured composite structures. The determination of void content is indirect, calculated from the measured density of a cured laminated part and the percent composition and theoretical densities of the constituents (Pebly 1987). This section will detail the techniques used to determine the void content of some of the graphite-reinforced/AMB-21 polyimide tubes fabricated using the resin transfer molding methods earlier described.

ASTM D 2734 - 70 *Standard Test Methods for Void Content of Reinforced Plastics* (Storer 1993) was used as the guide for determining the percentage of voids in the four tubular samples subjected to mechanical tensile and torsion testing. The ASTM test method is specifically developed for the testing of composites in which the effects of ignition on the constituents are known (fiberglass composites), but has been adapted for this study in which the digestion process was used to determine the weights of fiber and matrix in the samples. This is possible because the effects of the digestion process were determined and accounted for. The test method requires the densities of the neat resin, the reinforcing fibers, and the fabricated composite. The density of the resin ( $1.27 \text{ g/cm}^3$ )

was supplied by Daniel Scheimen (1996), the density of the fibers is available from data supplied by the fiber manufacturer ( $1.82 \text{ g/cm}^3$ ) and included with each roll of braid, and the density of the composite samples was determined using Archimedes method described in the previous section. After the digestion of the sample, the fiber and resin contents can be determined and a theoretical composite density may be calculated. This theoretical density is compared to the actual measured density of the samples and the difference in densities indicates the void content.

The theoretical density of a composite sample can be computed using the following formula:

$$T_d = \frac{100}{\left(\frac{R}{D} + \frac{f}{F}\right)}$$

Where,

$T_d$  = theoretical density of the composite

$R$  = resin in composite, weight percent

$D$  = density of resin

$f$  = fiber reinforcement in composite, weight percent, and

$F$  = density of fiber reinforcement.

This theoretical density is used to calculate the void content by the equation:

$$V = \frac{100(T_d - c)}{T_d}$$

Where,

$V$  = void content, volume percent, and

$c$  = measured composite density.

Note that dividing the two densities gives the fraction of material missing, a unitless ratio which may be interpreted as a weight or volume fraction. By convention, when discussing voids the missing fraction is almost always expressed as a volume. The test standard also notes that large voids with nonuniform distribution may cause considerable variation among samples, and increased void contents may require larger specimen sizes if any reasonable level of repeatability is to be expected.

### 3.9 Mechanical Testing

Mechanical testing is generally destructive testing designed to determine the properties of a material that are associated with elastic and inelastic reactions when force is applied, giving a relationship between stress and strain. This section will describe the fixtures and machinery used to subject the fabricated composite tubes to tensile and torsional loadings, as well as the methods used to collect data for the plotting of curves of stress versus strain for these loadings.

Mechanical testing consisted of tension and torsion analysis of several composite tubes using an axial torsion material test system model number 319.25 manufactured by MTS. The test unit had a force capacity of 250 kN (55 kip). The composite tubes were held with MTS 646 hydraulic collet grips of 2.00" capacity. The collet grips had a force

capacity of 250 kN (55 kip) in the axial direction and 2200 N·m (20,000 in·lbs) in the torsional direction. The collet grips were controlled by an MTS grip control unit model 685.10, capable of supplying 69 Mpa (10,000 psi) maximum pressure to the grips. The hydraulic actuator affixed to the test frame was also manufactured by MTS, model number 319.25S, and is capable of supplying a force of 250 kN (55 kip) through an effective area of 126.7 cm<sup>2</sup> (19.6 in<sup>2</sup>). The actuator was of a hydrostatic design with a static stroke of 162.6 mm (6.40") and a dynamic stroke of 152.4 mm (6.00"). The MTS hydraulic power supply had a rated working pressure of 207 bar (3000psi) at a flow of 80.3 liters/min (21.2 gal/min). MTS also supplied the Test Star Control software that applied the loadings through a preset program input before the tests began. Data acquisition was through a Labtech Notebook program running on an IBM compatible 286 personal computer, collected into a Lotus 1-2-3™ spreadsheet. Data was recorded from each of the six strain gauges attached to the part at a rate of once per second.

Both tensile and torsion tests were conducted in two sequential parts: first the tube was stressed to less than half of the ultimate breaking load and the load was removed, then loading was increased until the tube ruptured. All loadings were carefully controlled, using loading rates of twenty pounds per second for the tensile tests and twenty inch-pounds force per second for the torsional tests. The tensile tests were run under load control and torque control, meaning that the test apparatus applied a specified increasing or decreasing loading, no matter how far apart the grips had to move to sustain the loading rate, and the measured torque on the composite tube was maintained at zero, even

if the grips had to rotate to accomplish this. The torsional tests were run under the same conditions of load and torque control, but because the torque loading was specified the grips rotated in varying amounts and the axial loading was maintained at zero, even if the grips had to move closer or further apart from each other.

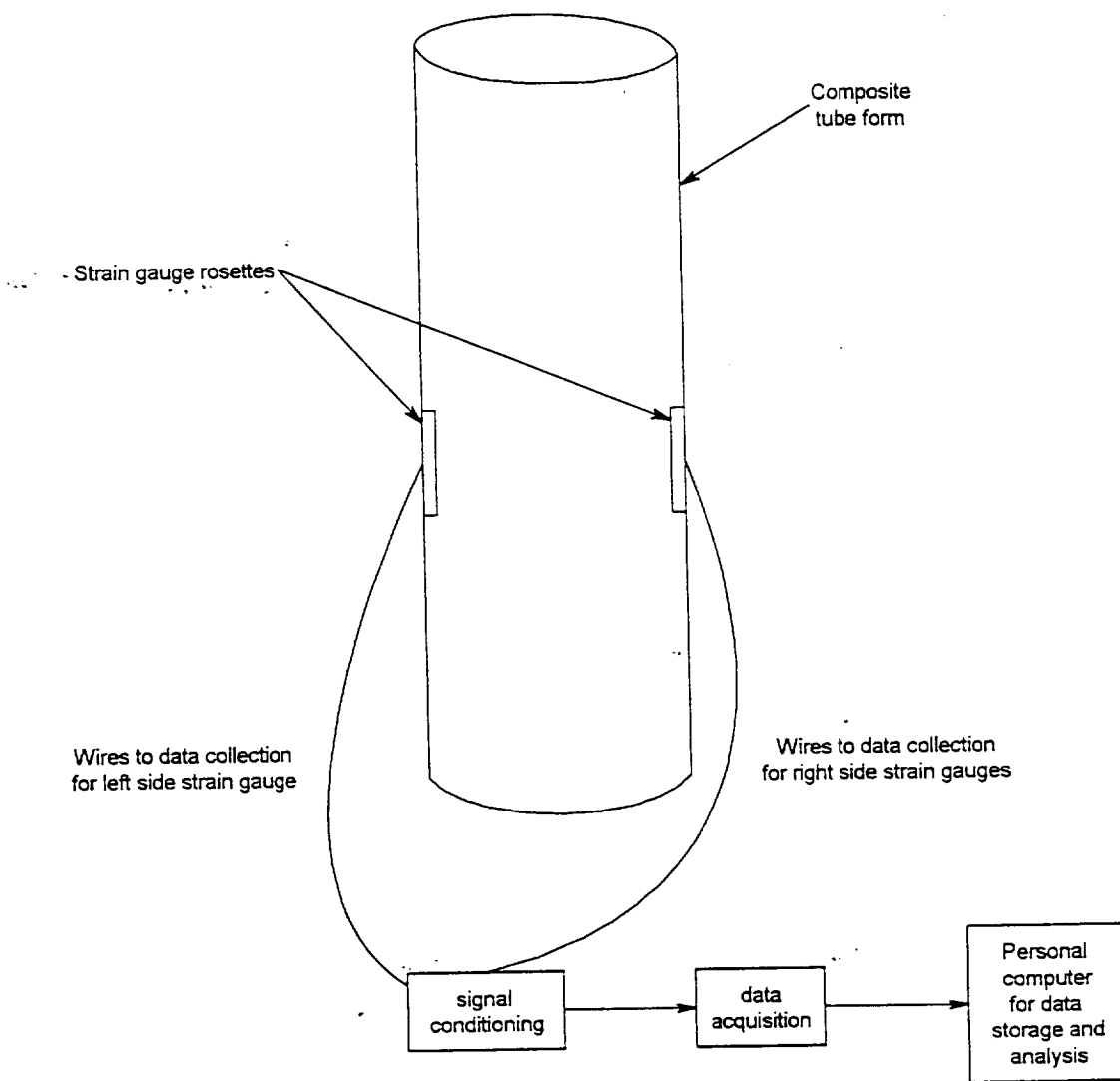
The collet grips were designed to accept a tube of 2.000" in diameter, although a tube of slightly larger outside diameter (about 2.020" maximum) could be fitted into the collet. The hydraulic power unit supplying energy to the grips was set at 3500 psi for each test. In order to prevent the composite tubes from being crushed by the collet it is necessary to plug the interior of the tube with a solid aluminum cylinder two inches long (or as long as the grip zone) custom fitted to each end of each composite tube. Because of the varying interior dimensions of the tubes some backing plugs varied in diameter. A table of the diameters of the backing plugs is presented below.

**Table 4.1:** Backing plug diameters for mechanical testing.

Tube Number	Top Plug		Bottom Plug	
	Toward End of Tube	Toward Center of Tube	Toward Center of Tube	Toward End of Tube
T-8	1.871"	1.864"	1.859"	1.869"
T-9	1.872"	1.867"	1.873"	1.878"
T-10	1.848"	1.834"	1.860"	1.868"
T-14	1.856"	1.856"	1.864"	1.865"

Strain gauges were applied to each tube to convert the physical movement of the tubes to a varying voltage, which could be correlated to the amount of strain actually

experienced by the tube directly under each strain gauge. As the tube was pulled or twisted, the strain gauges glued to the tube were also pulled or twisted, and the length of the strain gauge element changed minutely. This small change in the size of the gauge element causes the resistance of the strain gauge to change, and this variable resistance is used to vary the millivolt signal to the data acquisition software. The two precision strain gauges glued 180° apart (arbitrarily called left and right) on each tube were type CEA-06-250UR-350 manufactured by Measurements Group, Incorporated located in Raleigh, North Carolina. Figure 3.13 illustrates the relative positioning of the two strain gauge rosettes on the composite tube and the connections to the data collection devices. Each strain gauge rosette consisted of three individual strain gauges mounted at 0°, 45°, and 90°. The tubes were scuffed with fine sandpaper, cleaned with M-Prep Conditioner A (which was then neutralized with M-Prep Neutralizer 5A), and then the gauge rosettes were glued on with M Bond 200 adhesive after the area had been exposed to 200 Catalyst B. No varnish, shellac or other coating was applied over the gauges. Six very fine wires were soldered to the strain gauges to enable connection to the signal conditioner.



**Figure 3.13:** Positioning of strain gauges for mechanical testing.



## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.0 Introduction

The techniques detailed in the third chapter were used to formulate several batches of resin, which were in turn used to construct several composite tube forms. The tubes were fabricated using outer molds of drawn-over-mandrel (DOM) steel pipe as well as a clamshell-type two piece outer mold of aluminum construction. Six composite tubes of approximately eight inches length and one tube of approximately fifteen inches length were fabricated using the DOM pipe for the outer mold, while two composite tubes approximately twenty-four inches long were made using the clamshell mold. All of the tubes may be considered thin-walled because the ratio of the tube diameter to the approximate wall thickness is 32 to 1 (i.e. 2" to 1/16"), well above the minimum ratio of 10 to 1 that distinguishes thin-walled tubes from other types.

This chapter will present the results of viscosity measurements performed on each batch of resin. The percent of solids and the percent of solvents in the standard solution was determined and will be presented. Assorted methods of thermal analysis were also performed on samples of neat resin and small sections of completed composite tubes to determine the physical characteristics and processing parameters of the resin matrix, and the results of these tests will also be given. Several types of physical tests were performed on the fabricated tube forms, the results of which will be supplied. Information on specific gravity and percent fiber volume for most of the composite tubes will be given.

Mechanical test information including ultimate load at failure and stress-strain curves from both tensile and torsion testing for four of the short tubes will be shown, as well as photographs to illustrate the structural failure modes. One small sample of composite tube was sent to NASA Lewis Research Center in Cleveland, Ohio for determination of the glass transition temperature both before and after the post-cure cycle detailed in chapter three, and this information will also be supplied.

This chapter presents the results of the actual tests and all analysis and discussion of the results of these tests. Two qualifications should be noted, particularly with regard to the mechanical test data: the lack of post-curing and the small number of tubes actually tested. The specimens subjected to mechanical testing were not post-cured, therefore the cross-linking reaction did not go to completion and the strength of the parts is almost certainly lower than it could be, although the non-post-cured parts may be somewhat less brittle. The small number of samples subjected to the mechanical test program rules out any statistical analysis of the ensuing data. Because each tube was made using different techniques and processing parameters in the attempt to establish a standard procedure, the results from the mechanical testing must be viewed as an estimate of the strength of the composite parts made with this process. It is felt, however, that as the fiber alignment and processing of the tubes becomes more standardized, the strength of the parts will increase.

## 4.1 Characterization of Physical Properties

The physical properties of the resin solution and the resulting composite tubes were determined using test equipment at North Carolina A&T State University and the NASA Lewis Research Labs in Cleveland, Ohio. The resin solution was tested for viscosity and percent solids and further characterized by FTIR and the thermal testing methods of DSC, TGA, and TMA. Specific gravity, fiber volume and void volume testing were also performed. The results of the tests are presented in this section.

### 4.1.1 Results of Viscosity Measurements and Percent Solids Determination

Several small batches of resin were prepared using the methods described in chapter three. The viscosity of each batch at approximately 25 °C (77 °F) was determined using a Brookfield Rheometer Model DV-III equipped with Rheocalc data acquisition software and an LV-2 spindle. The temperature of the sample was maintained by the use of a constant temperature water bath also manufactured by Brookfield. The amount of solvent used to prepare each batch with the resultant viscosity of the batch is presented as Table 4.1.

**Table 4.1:** Results of viscosity measurements for monomeric resin solutions.

Batch Number	Mix date	Viscosity check date	Acetone (gm)	Temp (°C)	Spindle (RPM)	Torque (%)	Viscosity (cP)
B1	02/15/96	02/16/96	100.0	24.5	20.0	73.2	1098.0
B1	02/15/96	02/16/96	150.0	24.0	65.0	99.3	458.2
B2	03/23/96	03/29/96	150.0	25.0	49.0	99.1	606.6
B3	05/18/96	05/19/96	150.0	24.3	59.0	98.9	502.8
B4	05/28/96	05/31/96	150.0	24.2	46.0	99.5	648.8
B5	05/28/96	06/01/96	150.0	23.6	43.0	98.9	689.9

The effects of time and solvent concentration are readily apparent from the table. The addition of 50.0 gms of acetone to the B1 batch of resin lowered the viscosity from 1098 to 458 cP. If a resin batch was checked the day after preparation the viscosity could be expected to be about 400 -500 cP, as shown by batches B1 and B3. If several days are allowed to elapse, however, the viscosity of the resin can be expected to climb to about 600 - 650 cP, as shown by batches B2 and B4. Comparing batches B4 and B5, which were made on the same day and in the same proportions, it can be seen that one additional day at room temperature has increased the viscosity by about 40 cP. This increase in viscosity is due to the formation of short chain oligomers as the mixture becomes slightly imidized at room temperature.

Tests of the weight percentage of solids for three distinct batches of resin were performed by weighing small portions from each batch and placing into small glass vials. The samples were vacuum dried for one hour, then heated to 91 °C (196 °F) and allowed to dry under heat and vacuum overnight. The following morning the samples were removed from the vacuum oven and weighed. The calculated weight percent of solids in each resin batch are given as Table 4.2.

**Table 4.2:** Percent solids of selected monomeric resin solutions.

Batch Number	Wet Sample Weight (gm)	Dried Sample Weight (gm)	Percent Solids (%)
B3	16.8	13.1	78.0
B4	24.0	18.7	77.9
B5	20.7	16.2	78.3

The average and mean weight percentage of solids in the three samples was 78.1, giving an average weight percent of solvents of 21.9. The standard deviation ( $\sigma_s$ ) for the weight percent of solids is calculated to be 0.17 gms. High concentrations of solids are desirable because any excess solvent used to lower the viscosity of the mixture must be removed from the mold cavity after the resin has been transferred.

#### 4.1.2 Results of Resin Characterization and Thermal Testing

Results of tests conducted by Fourier Transform Infrared Analysis (FTIR) on two samples of resin, one a mixture of monomers and the other partially imidized by thermal treatment, are presented as Figures 4.1 and 4.2. Figure 4.1 is an FTIR analysis on a small sample of resin batch B5 that was dried to remove the acetone and excess methanol solvent at room temperature in a vacuum oven until no further weight loss could be detected. This sample received no thermal treatment other than minimal exposure to room temperature during the formulation, determination of viscosity, and drying of the resin batch. Figure 4.2 is the result of an FTIR analysis on a small sample of resin batch B3 that was also vacuum dried at room temperature for one hour then placed in a 53 °C (127 °F) overnight, followed by twenty-four hours exposure to 121 °C (250 °F). This thermal treatment partially imidized or partially "B-staged" the sample, changing the color from a golden yellow to a much darker brown. The plots are very similar except for the spike at the 780 nm wavelength present in the sample that has been partially imidized but not in the sample that has received minimal thermal treatment. This particular wavelength is characteristic of the imide ring structure. The presence of the spike at 1780 nm indicates

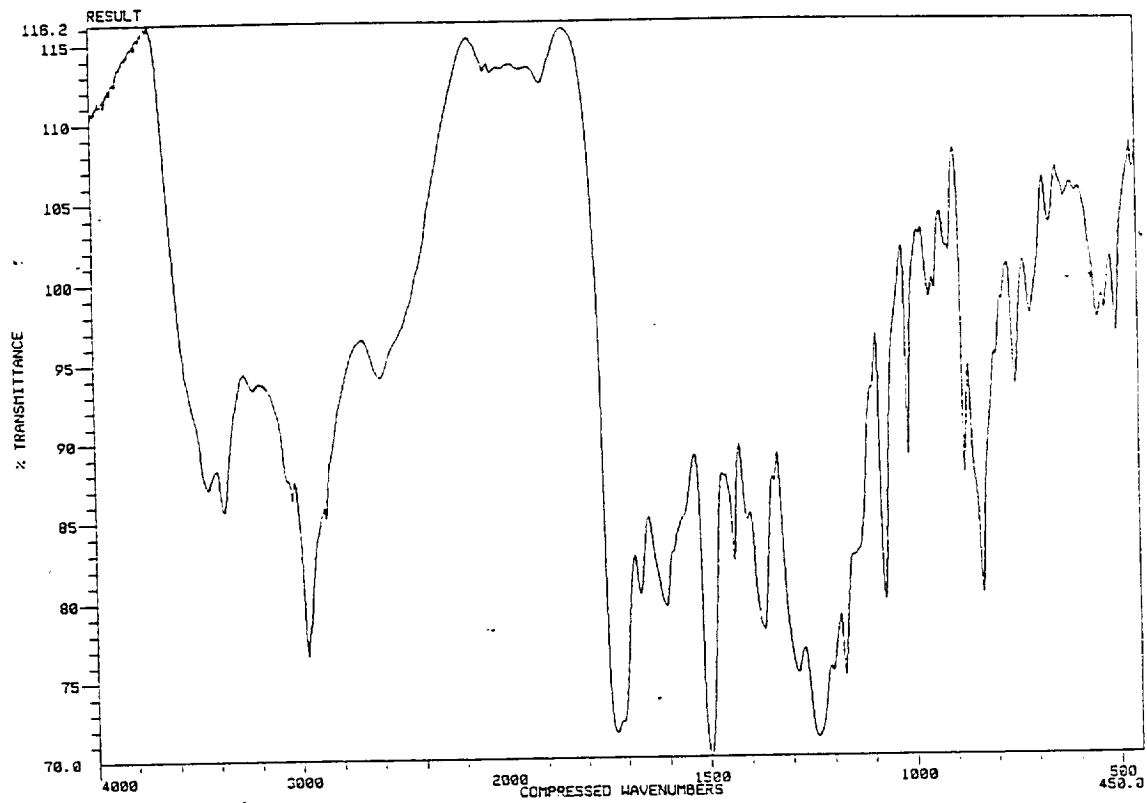
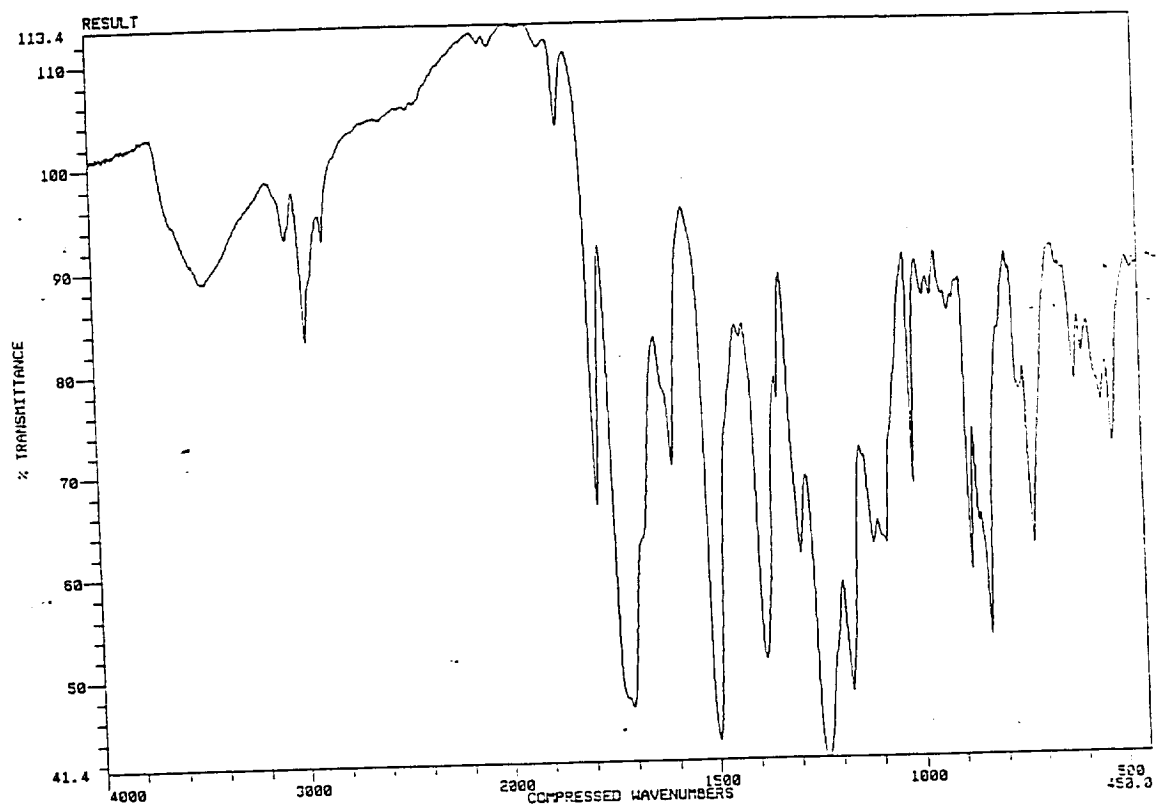


Figure 4.1: Fourier Transform Infrared analysis of resin batch B5.



**Figure 4.2:** Fourier Transform Infrared analysis of resin batch B3.

that the thermal treatment has initiated the growth of imide ring structures that were not in the initial sample.

Differential Scanning Calorimetry (DSC) testing was performed on a small 9.679 mg sample of resin batch B3 which had been vacuum dried for one hour at room temperature then placed in a 53 °C (127 °F) for twelve hours to remove as much solvent as possible. This mild thermal treatment probably advanced the imidization a small amount, but there was minimal color change to the sample caused by the drying. Nitrogen gas at a pressure of 1380 kPa (200 psi) was introduced into the test chamber to mimic the fabrication process and minimize the escape of cyclopentadiene during the cross-linking phase of the reaction sequence. The results of the analysis are presented as Figure 4.3. Below 100 °C (212 °F) there is a sharp endothermic heat loss because of the vaporization of methanol and acetone solvent which creates an evaporative cooling effect. Between 100 °C and 230 °C (212 °F and 446 °F) the imidization reaction is occurring and the oligomers are being formed; the condensation products are negatively sloped or endothermic because of the evaporative cooling effect while the positive sloped sections of the graph are indicative of oligomer growth to a more ordered state. Note that overall the reaction remains endothermic. Between 300 °C and 350 °C (572 °F and 662 °F) an exothermic crosslinking addition-type reaction is occurring at the reactive end caps, and there is no condensation product evolution and subsequent evaporation to draw the curve into the endothermic (negative) region. At 350 °C (662 °F), however, there is a small



DSC (HP)  
PL Thermal Sciences

SMPL ID : 051896 AMB-21  
RUN ID : dried 53C ~12hr  
SIZE : 9.679 mg  
OPERATOR: DAS

DATE RUN: Jun/06/1996  
GASES : N2 200PSI  
SOURCE : Dan  
COMMENT :

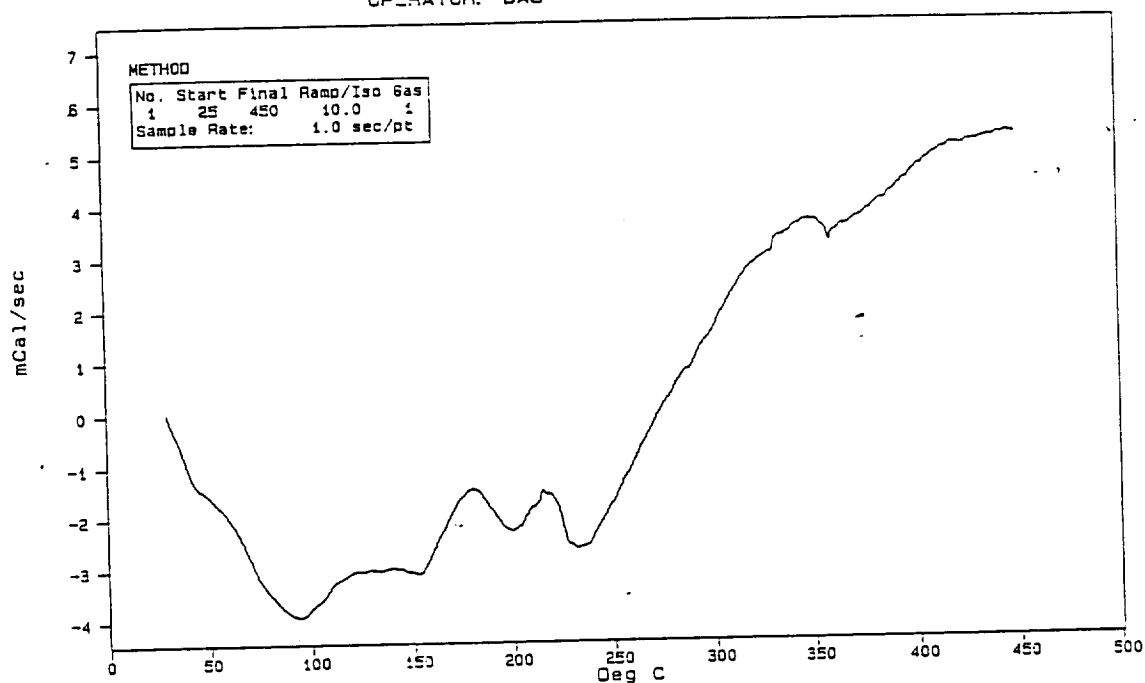


Figure 4.3: Differential Scanning Calorimetry analysis of resin batch B3.

bump downward which is believed to be the evolution of cyclopentadiene, a product of the nadic ester cross-linking reaction.

Thermogravimetric analysis (TGA) was performed on a 9.116 mg sample of resin batch B4 to determine the percent weight loss as the sample temperature was raised at a constant ramp rate of 10 °C (18 °F) per minute. The sample was prepared by drying a small amount of resin solution overnight under a strong vacuum then heating the sample to 53 °C (127 °F) for a period of twelve hours. Nitrogen gas at a flow rate of 60 cm<sup>3</sup>/min was used as a sweep gas to remove imidization and volatile decomposition products created at the higher temperatures. The results of the TGA, plotted as percent weight loss versus time, are presented as Figure 4.4. The percent weight loss below about 100 °C is due to the loss of water, acetone and methanol as the powdered resin dries completely and the imidization reaction begins to occur with by-product evolution. Above a temperature of about 120 °C (248 °F) the rate of the imidization reaction increases and more condensation products are evolved as evidenced by the sharp downturn in the slope of the line. About 250 °C (482 °F) the slope of the line flattens out a bit indicating that the bulk of the imidization reaction and by-product evolution has occurred. Weight loss due to thermal decomposition occurs rapidly above 480 °C (896 °F), and the final product weighs about 41% of the original starting weight. Note that this test was run under inert nitrogen, if oxygen had been allowed to react with the sample the final percent weight would have been much lower, as nothing would have remained but ash.

TGS-II  
PL Thermal Sciences

SAMPLE ID : AMB-21 Monomer  
RUN ID : Dried powder  
SIZE : 9.116 mg  
OPERATOR: DAS

DATE RUN: Jun/04/1996  
GASES : N2 60 cc/min  
SOURCE : Dan  
COMMENT : A 052896

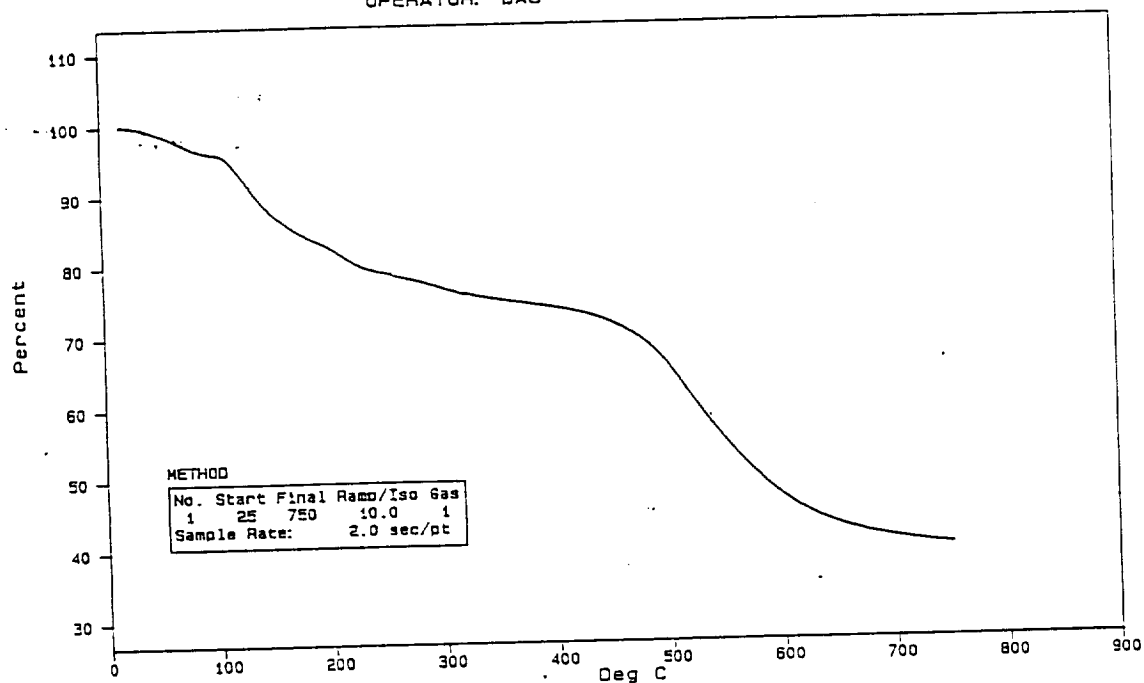
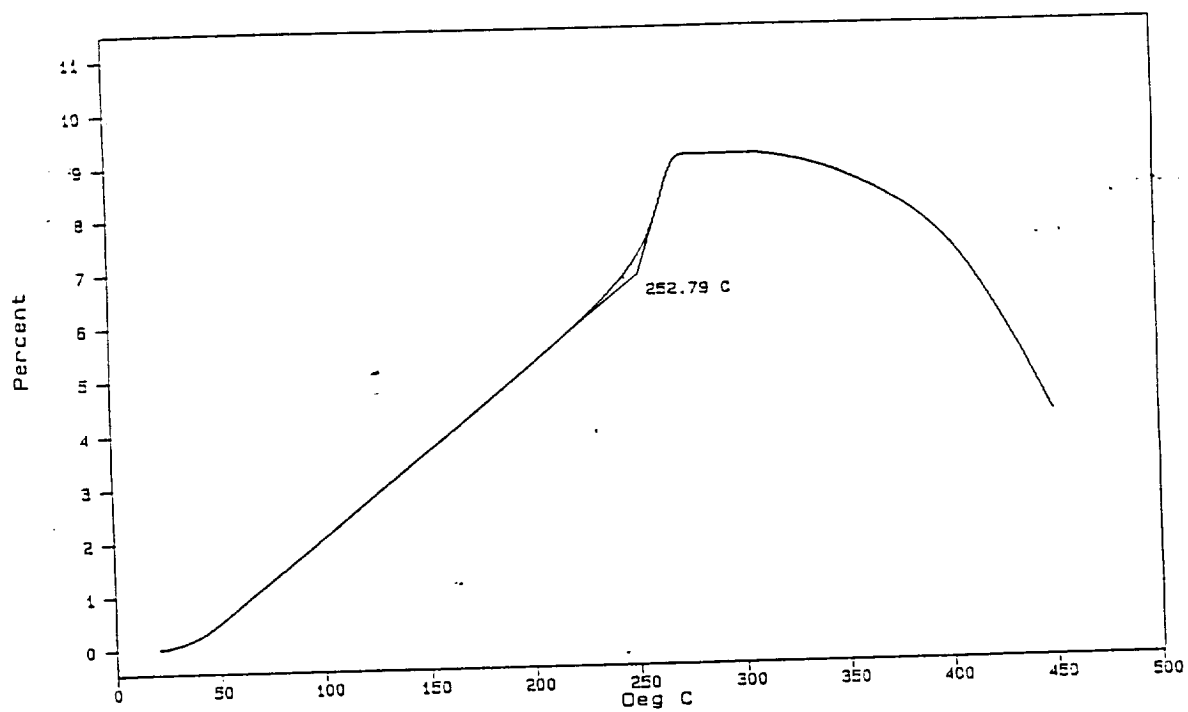


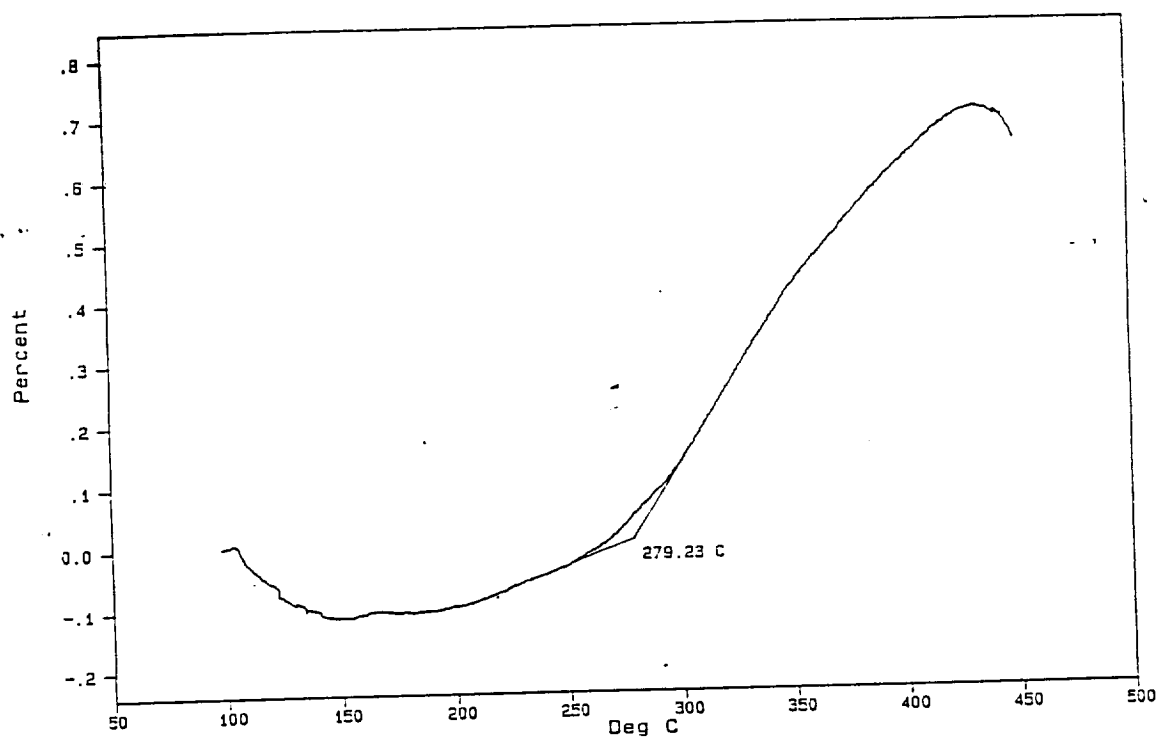
Figure 4.4: Thermogravimetric analysis of resin batch B4.

Thermomechanical analysis (TMA) was conducted on two samples from composite tube number T-12 in order to determine the glass transition temperature ( $T_g$ ) both before and after a post-cure cycle. Both tests were conducted in air and used an increasing temperature ramp rate of 10 °C per minute for the entire run. The tests were run between room temperature and 450 °C (842 °F). The non-post-cured specimen exhibited a  $T_g$  of 252.79 °C (487 °F) while the post cured sample's  $T_g$  was elevated to 279.23 °C (534.6 °F). Plots of the thermographs are shown as Figures 4.5 and 4.6. The rise in the glass transition temperature is thought to occur because of the increased density of cross-linked sites throughout the matrix, resulting in bonds that are much more rigid and less free to rotate.

The percent weight loss due to the post-cure cycle for a three-inch section of tube was also determined. The composite sample weighed 39.5977 gms before the post-cure cycle was begun, and 38.5740 gms after the cycle. Both weights were determined by heating the sample in an oven to 100 °C (212 °F) while exposing the sample to a strong vacuum for a period of 16 hours, then turning off the heat source and allowing the sample to cool while maintaining the vacuum for another 24 hours, then weighing as quickly as possible. The weight loss for this sample due to the post cure thermal treatment is calculated to be approximately 2.6 %. This is consistent with the gradual slight weight loss at these temperatures exhibited by the TGA sample described earlier.



**Figure 4.5:** Thermomechanical analysis of tube T-12 before post-curing.



**Figure 4.6:** Thermomechanical analysis of tube T-12 after post-curing.

#### 4.1.3 Results of Specific Gravity Testing

The specific gravity of several entire tubes and small samples from selected tubes were determined by the method of Archimedes outlined in chapter three, which involves weighing the sample dry, obtaining the weight of the sample submerged in water at 25 °C (77 °F), and performing a simple calculation. The results of the measurements and the calculated specific gravities are presented as Table 4.3. The specific gravities of the selected tubes ranged from a low of 1.35 to a high of 1.52, with a mean of 1.43 and a standard deviation ( $\sigma$ ) of 0.045.

#### 4.1.4 Results of Fiber Volume and Void Volume Testing

Samples from several tubes were subjected to the sulfuric acid/hydrogen peroxide digestion procedure described in the previous chapter to determine the volume percent of reinforcement fibers, resin matrix, and voids in the composites. Two samples were cut from each tube after the destructive tests using a one and one-eighth inch (1-1/8") silicone carbide grit-edged hole saw, giving two samples of approximately one inch (1") diameter with a slightly bowed or curved shape. These samples were cut as close as possible to the ends of the tubes, but not from the region gripped by the collets or in a region where the fracture pattern had compromised the physical structure of the specimen.

A small (1.4269 gm) section of braided preform was also subjected to the digestion procedure at the same time and under the same conditions as the composite samples as required by the ASTM standard methodology. The preform fibers exhibited a net loss of 0.0200 gms, resulting in a 1.42 % weight loss. It is assumed that all of the fibers in the composite samples exhibited the same percent weight loss, therefore the fiber

**Table 4.3:** Specific Gravity measurements for fabricated composite tubes.

Sample number	Location	(a)	(b)	(w)	Specific Gravity
T-8	entire tube	82.8433	37.1530	13.8450	1.39
	top	1.1352	1.9800	1.6357	1.44
	bottom	1.2350	1.9589	1.6357	1.35
T-9	entire tube	77.0250	37.2190	13.8482	1.43
	top	1.1237	1.9713	1.6357	1.43
	bottom	1.1026	1.9860	1.6358	1.47
T-10	entire tube	72.7677	37.2006	13.8649	1.47
	top	1.2926	1.9682	1.6356	1.35
	bottom	1.2298	1.9950	1.6356	1.41
T-11	entire tube	78.8715	39.0330	13.8432	1.47
	top	2.5360	2.4182	1.651	1.45
	bottom	2.5354	2.5002	1.6350	1.52
T-14	top	1.1332	1.9762	1.6356	1.43
	bottom	1.1423	1.9885	1.6355	1.45

Where

(a) = weight of dry sample in grams

(b) = weight of sample in water with wire

(w) = weight of wire in water

$$\text{and Specific Gravity} = \frac{a}{a + w - b}$$



weight "W" was corrected for this loss. Multiplying the weight of the digested and dried fibers in the equation for the calculation of fiber volume by a factor of 1.014215651 accounts for the slight oxidation of the graphite fibers. This loss of weight may be attributed to the digestion of an epoxy sizing agent applied to the fibers to facilitate braiding, or possibly some small oxidation of the fibers themselves, although this is much less likely. The weight results of the digestions and the calculated fiber volume percentages are given as Table 4.4. Fiber volumes ranged from 44.3 to 61.2 percent, with a mean of 55.1 percent and a standard deviation ( $\sigma_n$ ) of 4.9 percent. Fiber volumes of 55 to 60 percent are generally considered to be very good.

The volume percent of voids in the tubes subjected to mechanical testing was also determined as outlined in chapter three using a value of 1.27 for the density of the neat AMB-21 resin and a value of 1.82 for the density of the AS4 graphite fibers. The weight percent of resin and fiber in each sample was determined and these were used to calculate a theoretical density for each sample. The mean weight percentage of graphite fibers in the specimens was 66.6, with a standard deviation ( $\sigma_n$ ) of 3.81 %. The mean weight percentage of matrix was 33.4. A comparison of the theoretical density to the actual measured density allowed for the determination of the percentage of voids in each of the eight samples. These results are presented as Table 4.5.

**Table 4.4:** Volume percentage of fibers in selected composite tubes.

Sample number	$W$ (corrected) (gm)	$\bar{r}$	$a$ (gm)	Specific gravity	$c$	Fiber, Volume %
T-8 top	0.7623	1.82	1.1352	1.4353	1.4317	53.6
T-8 bottom	0.7578	1.82	1.2350	1.3545	1.3511	46.2
T-9 top	0.7752	1.82	1.1237	1.4258	1.4223	54.7
T-9 bottom	0.7704	1.82	1.1026	1.4654	1.4618	56.9
T-10 top	0.7656	1.82	1.2926	1.3465	1.3431	44.3
T-10 bottom	0.7686	1.82	1.2298	1.4129	1.4094	49.1
T-11 top	1.7925	1.82	2.5360	1.4467	1.4431	56.1
T-11 bottom	1.8660	1.82	2.5354	1.5117	1.5133	61.2
T-14 top	0.7659	1.82	1.1332	1.4297	1.4262	53.7
T-14 bottom	0.7829	1.82	1.1423	1.4472	1.4436	55.1

Where

$W$  = bone dry weight of fiber in composite sample after digestion, corrected for effects of digestion

$\bar{r}$  = fiber density (1.82 for AS4 carbon fibers)

$a$  = bone dry weight of composite specimen

$c$  = composite density (0.9975 times the Specific Gravity at 23 °C)

$$\text{and Fiber, Volume \%} = \frac{\left(\frac{W}{\bar{r}}\right)}{\left(\frac{a}{c}\right)}$$

**Table 4.5:** Void volume percentage in tubes subjected to mechanical testing.

Tube number	Resin weight %	Fiber weight %	Theoretical density	Void volume %
T-8 top	31.89	68.11	1.60	10.47
T-8 bottom	37.77	62.23	1.56	13.62
T-9 top	30.03	69.97	1.61	11.69
T-9 bottom	29.14	70.86	1.62	9.55
T-10 top	39.93	60.07	1.55	13.44
T-10 bottom	36.61	63.39	1.57	10.28
T-14 top	31.45	68.55	1.60	10.97
T-14 bottom	30.49	69.51	1.61	10.21

Calculated void volumes ranged from 9.55 % to a high of 13.62 %, with a mean void volume of 11.3 % and a standard deviation ( $\sigma_n$ ) of 1.42 %.

Void volumes of 9 % to 14 % were considerably higher than hoped for. Some of this voidage can be attributed to areas of resin starved fibers, but the bulk of the void volume must be caused by small trapped inclusions or bubbles caused by volatile gases that did not diffuse out of the resin.

## 4.2 Characterization of Mechanical Properties

This section will present the results of the destructive mechanical testing carried out on a small sample of tubes manufactured by methods previously described.

### 4.2.0 Introduction

Although many properties can be measured by mechanical testing, the test program conducted on the tubular samples included measurements of tension and torsion properties only. Preliminary mechanical testing was conducted on eight to nine inch long sections

cut from tube T-15, which was fabricated in the two piece clamshell mold. Because of machining errors in the construction of the outer mold, this two piece aluminum assembly was bored oversize and the two halves did not line up precisely, resulting in a non-concentric composite part with an outer diameter that was too large to fit the hydraulic collets on the biaxial test frame. It was decided to use the composite tubes from the two piece clamshell mold to establish the testing parameters for the seamless composite tubes, which did fit into the collets properly. The outer diameter of the tubes made in the clamshell mold had to be sanded quite vigorously on the two inch region at each end gripped by the collets, which removed quite a bit of matrix material and cut into the braided fibers severely, sometimes removing an entire layer of preform. Obviously, the testing of these tubes would not be representative of the composite tubes made in the seamless DOM outer mold, but could be used to determine rates of loading and the approximate load at failure.

Tube T-15a was subjected to an increasing load of 10 lbs/sec and eventually broke in the grip region at a tensile load of approximately 16,500 lbs. The hydraulic pressure of 5,000 lbs/in<sup>2</sup> crushed the tube in the grip area, leaving significant markings on the tube. It was decided to lower the pressure in the collet to 3,500 lbs/in<sup>2</sup> for the next run. Tube T15c was subjected to an increasing torsional load of 20 in-lb/sec. The tube also broke in the grip region at a torque of about 13,000 in-lb, and the grip regions were only slightly marked from the pressure of 3500 lbs/in<sup>2</sup>. These two runs established useful benchmarks for subsequent testing.

#### 4.2.1 Torsion testing

Torsion testing was carried out on tubes T-8 and T-9, and the bi-axial test frame was programmed to keep the axial displacement at zero. Both tubes broke outside of the grip area, and the tests are considered valid. Photographs of the two broken tubes are displayed as Figures 4.7 and 4.8. Notice the characteristic spiral breakage pattern along the fiber direction and the areas where the strain gauges were attached. Load versus displacement and stress-strain diagrams for the T-8 specimen are given as Figures 4.9 and 4.10, respectively, while the same diagrams for the T-9 sample are shown as Figures 4.11 and 4.12. Tube T-8 broke at an ultimate rotational load of 12,553 in-lb<sub>r</sub>, corresponding to a rotation of 3.0052 degrees. In order to maintain the axial displacement at zero a compressive force of 102.9 lbs had to be applied by the test frame. Tube T-9 broke at an ultimate rotational load of 12,018 in-lb<sub>r</sub>, corresponding to a rotation of 3.2516 degrees. The test frame applied a tensile loading of 31.5 lbs to maintain the axial displacement at zero. Mechanical properties calculated from the test results are summarized in Table 4.6.

**Table 4.6:** Mechanical properties of tubular specimens subjected to torsion testing.

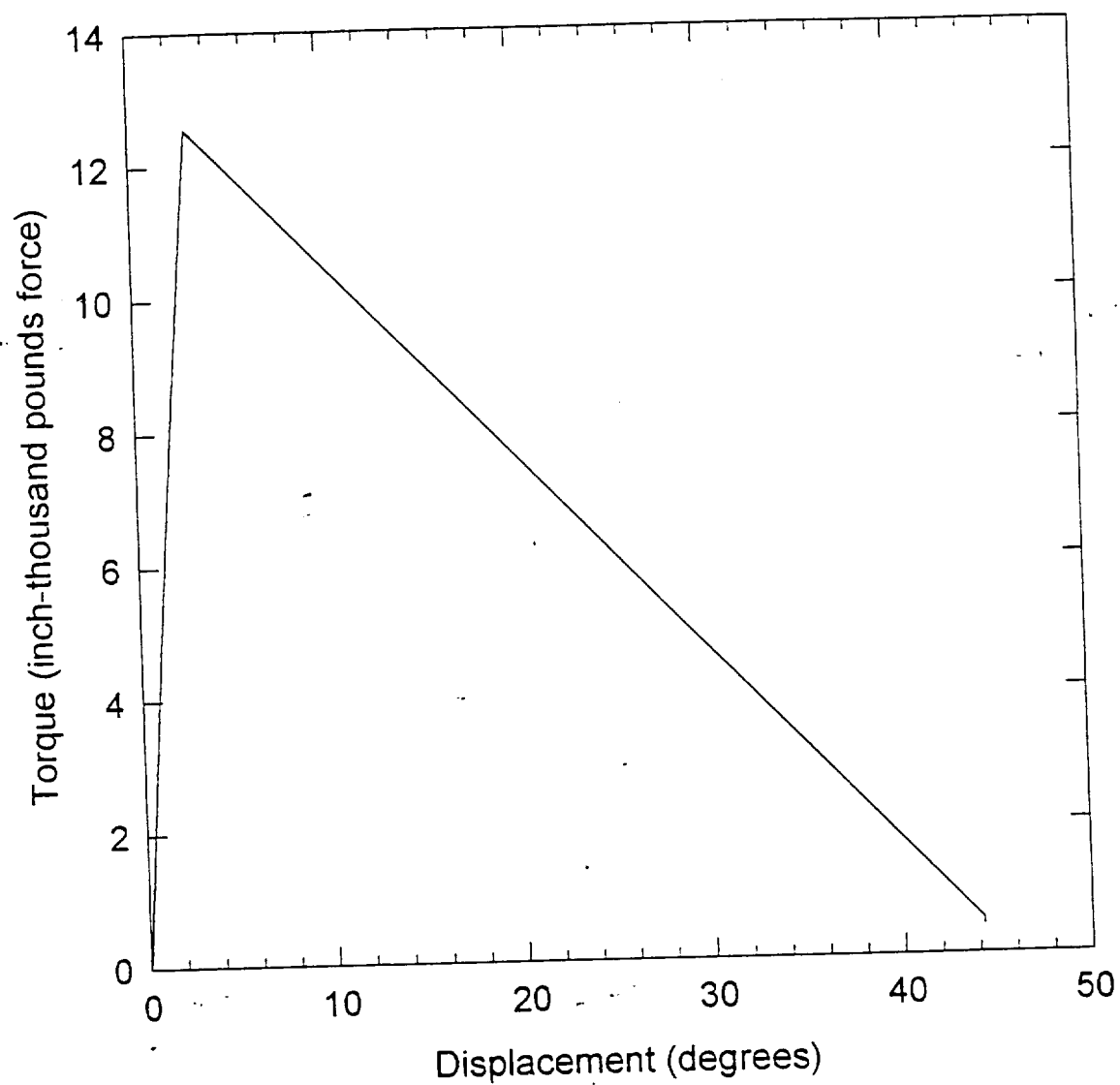
Tube number	Polar moment of inertia	Mean radius	Ultimate shear stress	Shear modulus
T-8	0.3888 in <sup>4</sup>	0.9651"	31158 lbs/in <sup>2</sup>	6.8 x 10 <sup>6</sup> lbs/in <sup>2</sup>
T-9	0.3761 in <sup>4</sup>	0.9673 "	31661 lbs/in <sup>2</sup>	6.7 x 10 <sup>6</sup> lbs/in <sup>2</sup>



**Figure 4.7:** Photograph of Tube T-8 after torsion testing.



**Figure 4.8:** Photograph of Tube T-9 after torsion testing.



**Figure 4.9:** Torque versus displacement plot for Tube T-8.



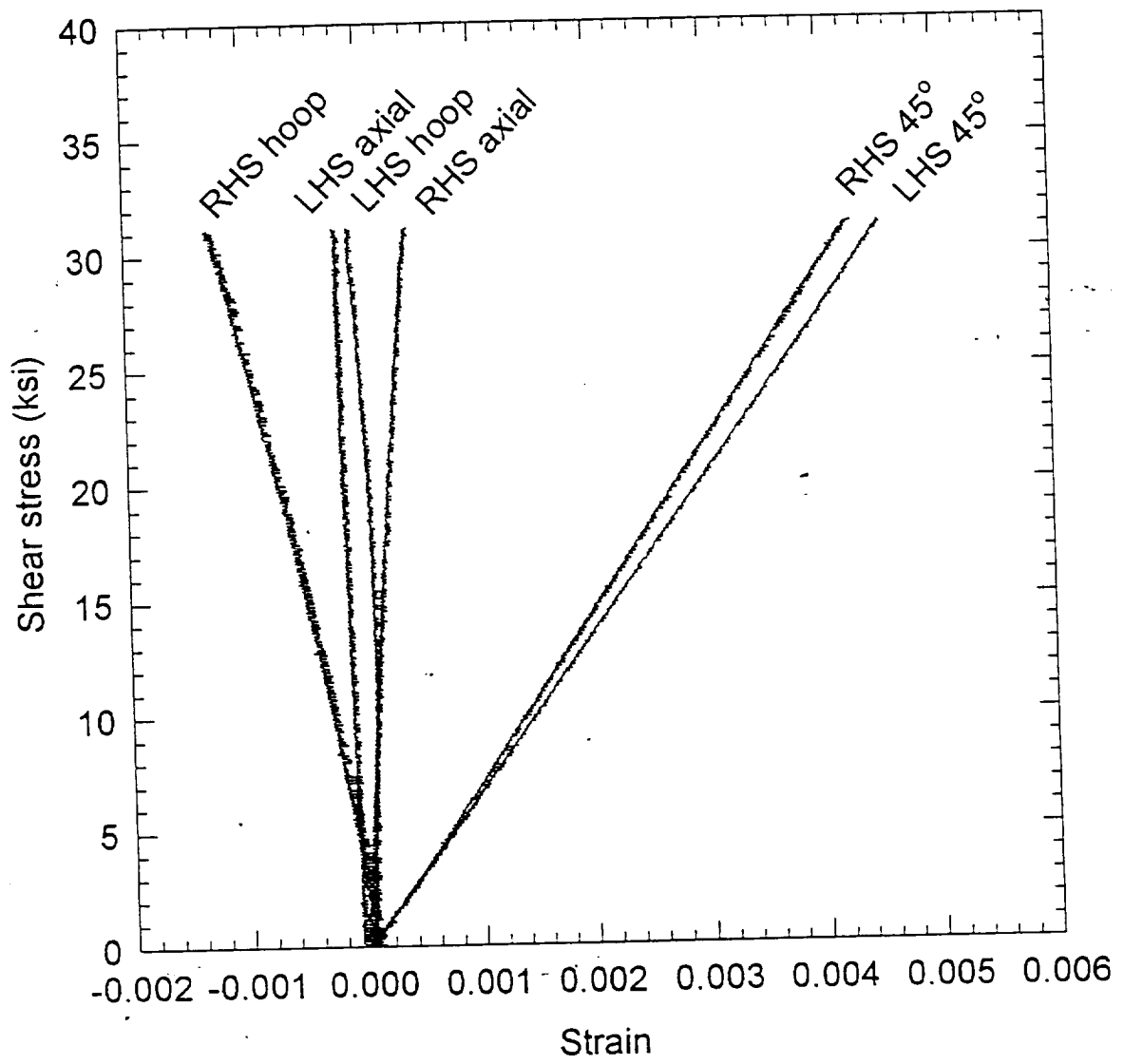
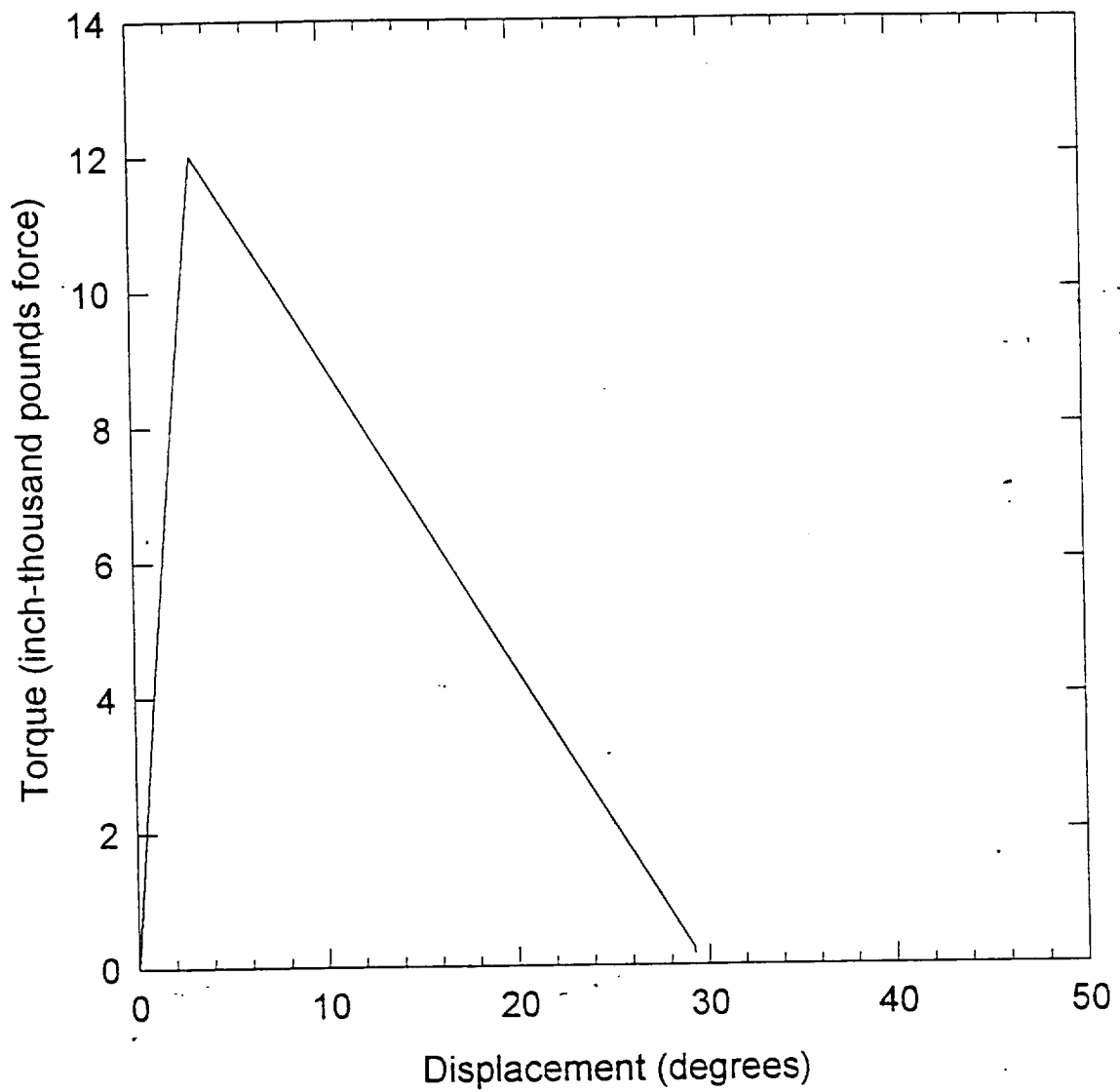


Figure 4.10: Stress - strain diagram for Tube T-8.



**Figure 4.11:** Torque versus displacement plot for Tube T-9.

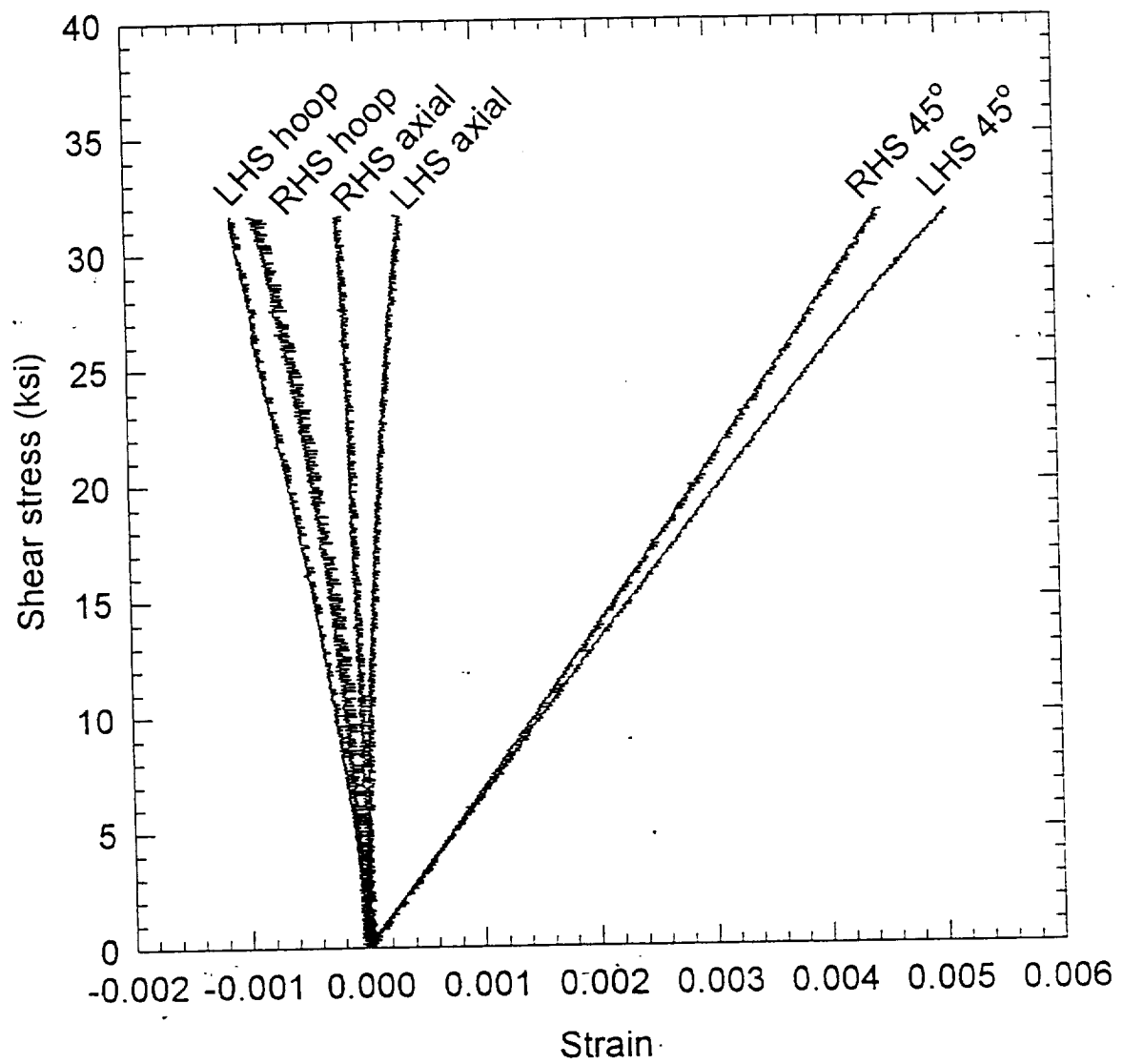


Figure 4.12: Stress - strain diagram for Tube T-9.

### 4.2.2 Tension Testing

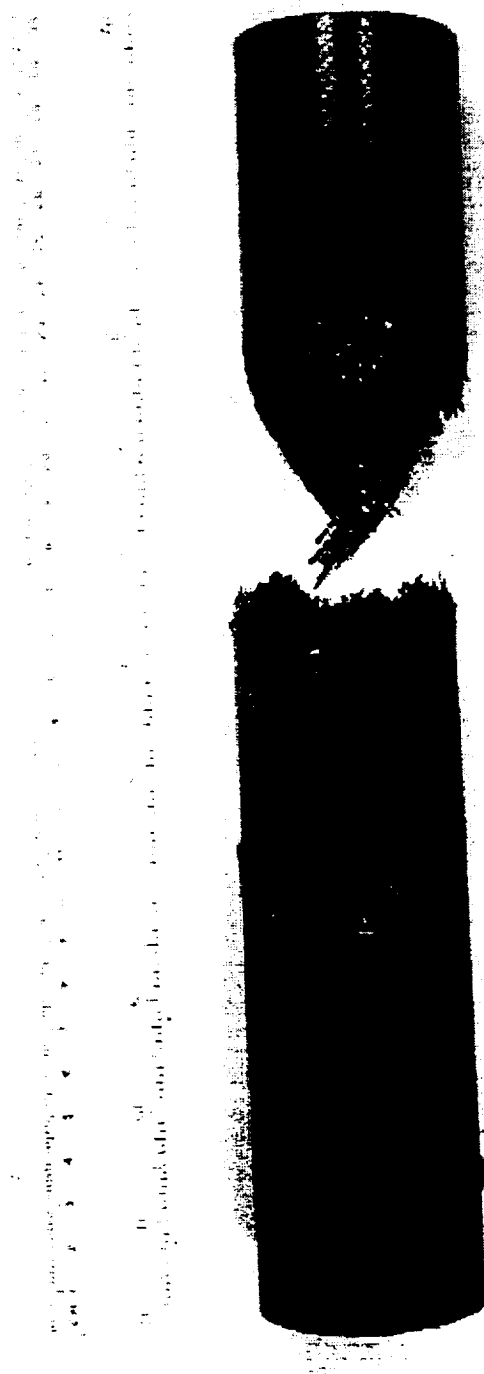
Tubes T-10 and T-14 were subjected to tensile loading while the test frame kept the rotational displacement at zero. Both tests are considered valid as the tubes broke outside of the grip area. Tube T-10 fractured at an ultimate tensile load of 19,435 lbs, breaking at an axial displacement of 0.284127". A force of 32.7 in-lb<sub>f</sub> was required to maintain a zero rotational displacement. Tube T-14 broke at an ultimate load of 15,827 lbs, corresponding to an axial displacement of 0.10252". A mere 16.2 in-lb<sub>f</sub> was needed to maintain the rotational displacement at zero. The calculated results of the mechanical properties are summarized in Table 4.7. Photographs of the broken tubes are shown in Figures 4.13 and 4.14, while Figures 4.15 through 4.18 are plots of the load-displacement and stress-strain curves for the two tubes.

**Table 4.7:** Mechanical properties of tubular specimens subjected to tensile testing.

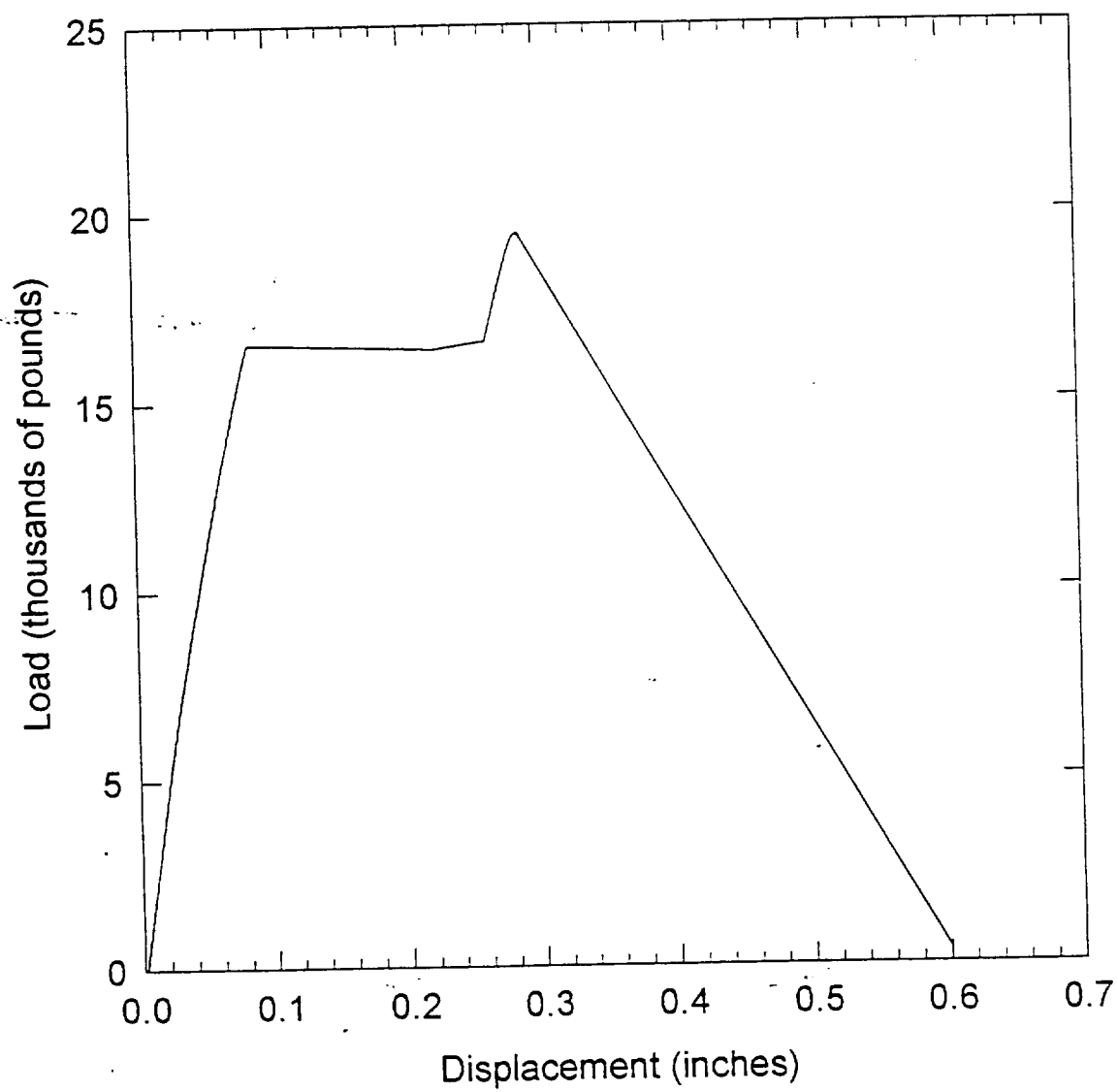
Tube number	Cross-sectional area	Ultimate failure stress	Modulus of elasticity	Poisson's ratio
T-10	0.459 in <sup>2</sup>	42,329 lbs/in <sup>2</sup>	3.1 x 10 <sup>6</sup> lbs/in <sup>2</sup>	0.91
T-14	0.421 in <sup>2</sup>	37,569 lbs/in <sup>2</sup>	3.1 x 10 <sup>6</sup> lbs/in <sup>2</sup>	0.92



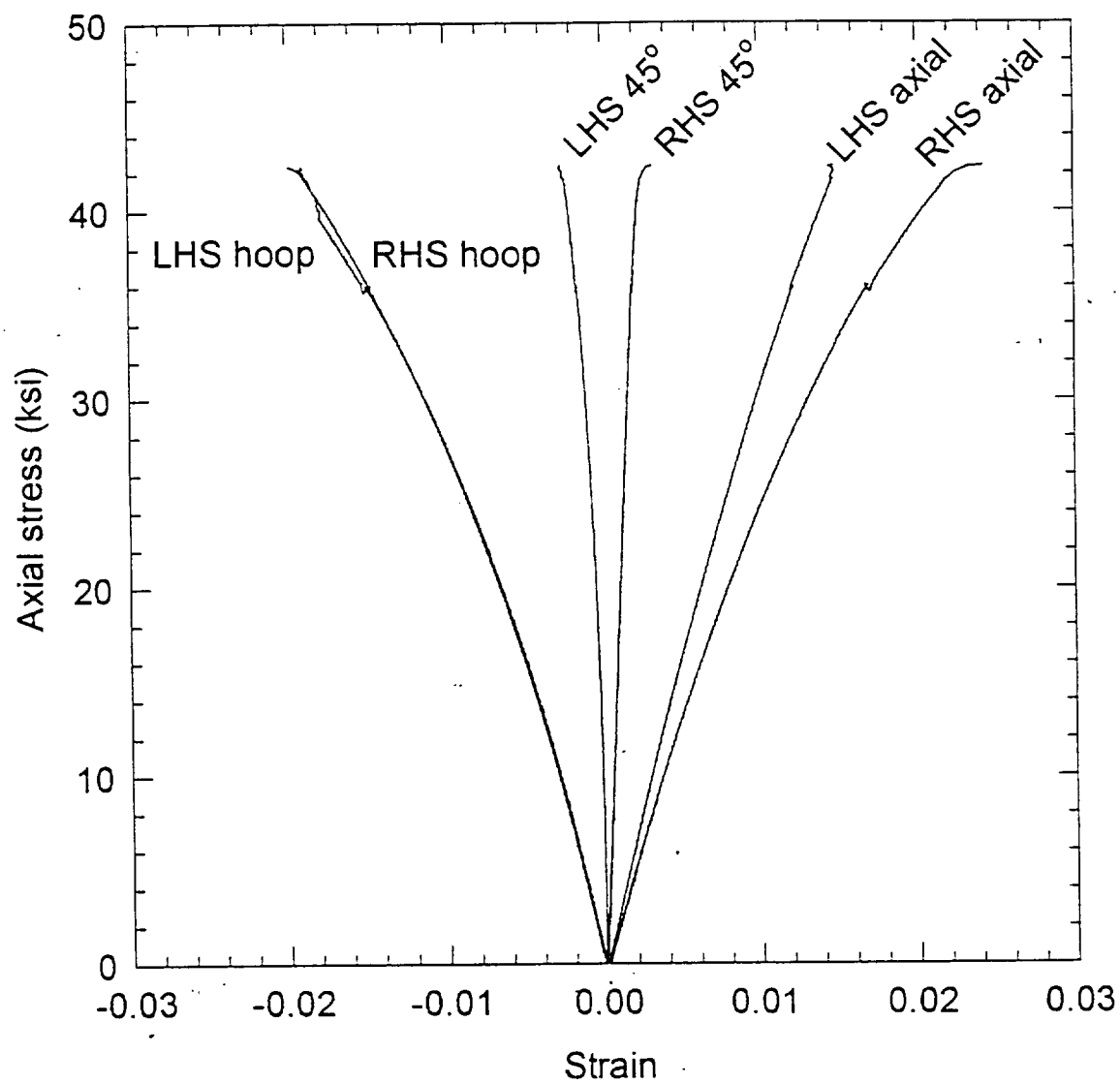
**Figure 4.13:** Photograph of Tube T-10 after tensile testing.



**Figure 4.14:** Photograph of Tube T-14 after tensile testing.

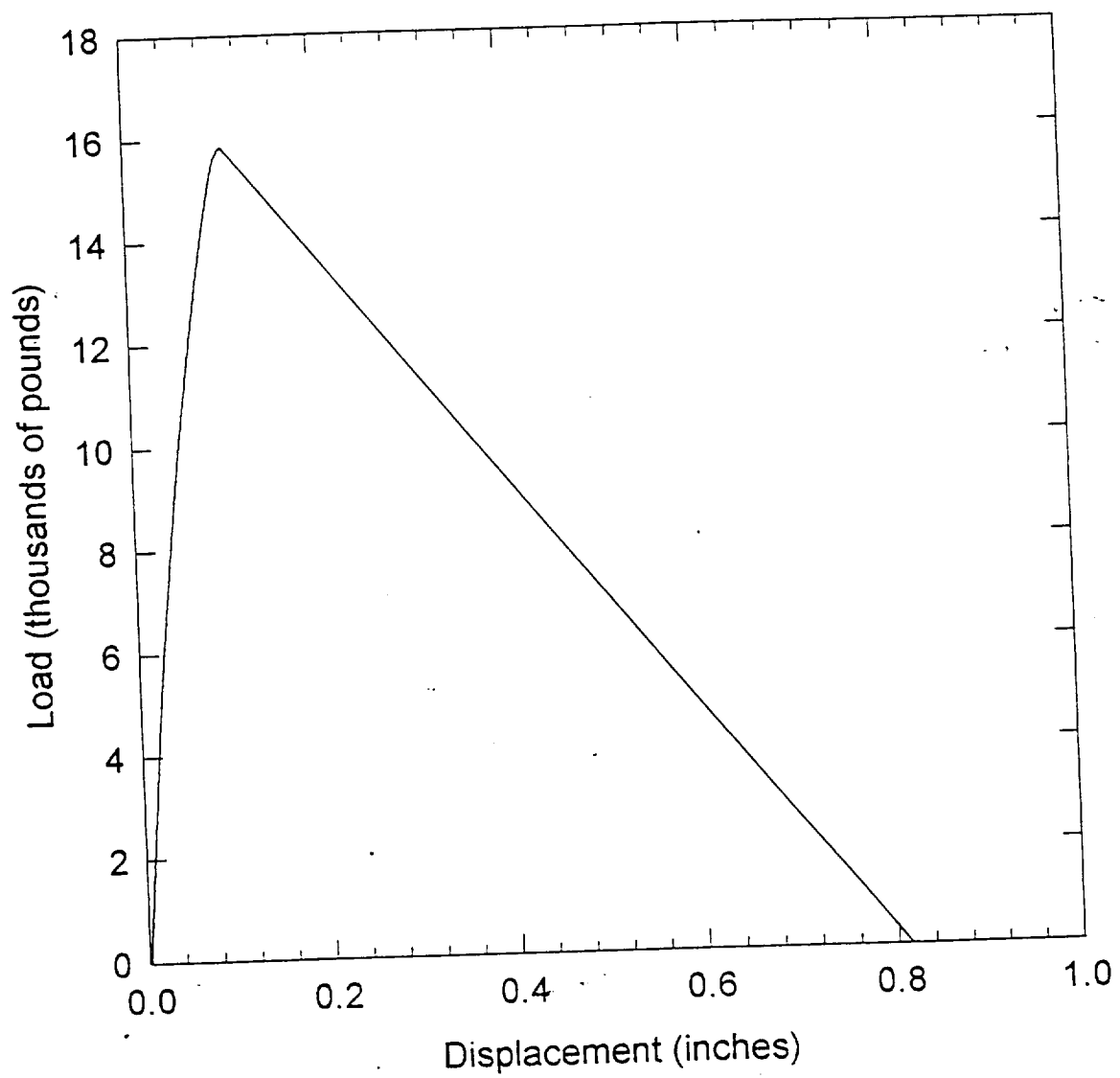


**Figure 4.15:** Load versus displacement plot for Tube T-10.

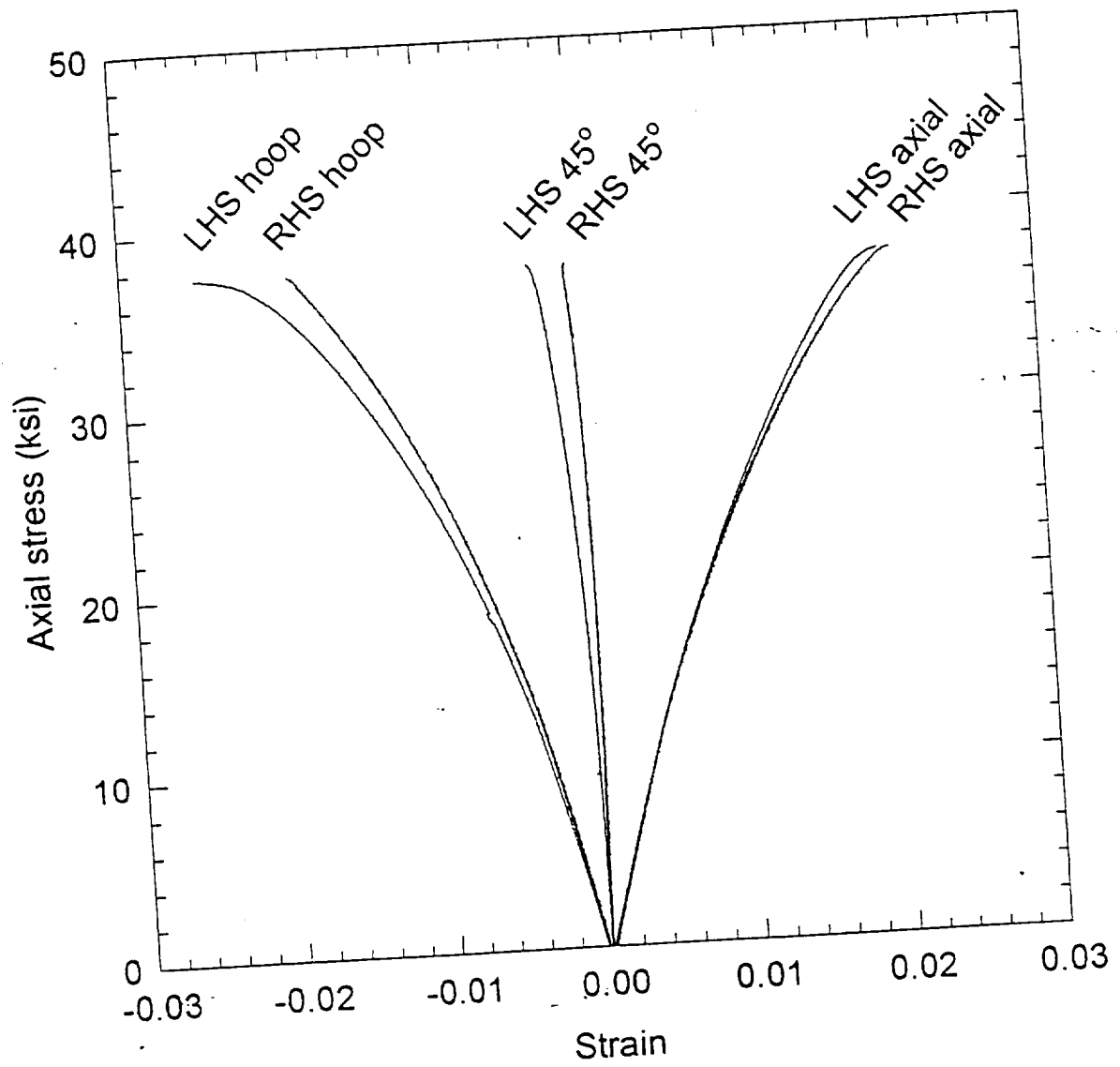


**Figure 4.16:** Stress - strain diagram for Tube T-10.





**Figure 4.17:** Load versus displacement plot for Tube T-14.



**Figure 4.18:** Stress - strain diagram for Tube T-14.

## CHAPTER 5

### CONCLUDING REMARKS

The techniques necessary for the fabrication of a complex three-dimensional tubular form using a PMR-type resin have been developed to allow for the construction of several tubes with good physical and mechanical properties. Employing established resin transfer molding practices, the relatively non-hazardous AMB-21 in acetone formulation was used to successfully impregnate four layers of AS4 braided graphite fiber preform previously loaded around an aluminum cylindrical core in an enclosed mold cavity. Using heat and vacuum, the solvent was evaporated to form a pre-preg followed by a partial imidization and removal of condensation products. The aluminum core was replaced by a silicone rubber bladder and the cure cycle continued to the final stage of 550 °F with a bladder internal pressure of 200 lbs/in<sup>2</sup> while simultaneously applying a strong vacuum to the prepreg for removal of any additional imidization products. A combination of several modifications to the standard resin transfer molding methodology enabled the mold to "breathe", allowing the imidization products a pathway for escape.

AMB-21 resin was chosen because of the carcinogenic nature of the primary commercial polyimide PMR-15. The AMB-21 resin was formulated using commercially available monomers or monomer precursors and dissolved in a mixture of methyl alcohol and acetone. The viscosity of the resulting monomer solution was checked by use of a Brookfield rheometer and adjusted by adding acetone to an easily pumpable viscosity of about 600 cP. In addition, several types of chromatographic and thermal analyses were

of the braids, and excess handling of the preforms broke some of the microscopic fibers, needlessly decreasing the strength of the finished part. In addition, three dimensional braided preforms with fibers along the length of the tube will be significantly stronger in tension than the braided preform used in this study.

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